Special Issue on Application of Science for Sustainable Development to Overcome Covid-19 Pandemic
Published by Novateur Publication India's
JournalNX- A Multidisciplinary Peer Reviewed Journal
ISSN: 2581-4230, Website: journalnx.com, 7th Aug. 2020

SYNTHESIS OF RESORCINOL VINYL ETHER IN THE MONO-POSITION, INFLUENCE OF THE CATALYST, TEMPERATURE AND SOLVENT ON THE REACTION YIELD

Olimov Bobir Bahodirovich
Bukhara state University, Teacher of the Department of Chemistry Uzbekistan,

Akhmedov Vokhid Nizomovich
Bukhara Institute of engineering technologies, Head of the Department of Chemistry, Ph. D., Associate Professor. Uzbekistan,

Rakhmatov Ziyodulla Shavkatovich
Bukhara state University. Bachelor Student of the Department of Chemistry Uzbekistan, Bukhara

Abstract

Currently, the synthesis of substances containing double and triple bonds solves a number of problems in the industry. But in the process of synthesis of these substances we are faced with some problems. This article discusses the influence of the catalyst and temperature on the synthesis of resorcinol and vinyl acetylene esters containing unsaturated bonds. Alkali metal hydroxides were chosen as a highly alkaline medium. Of the experimental variants, the highest result was observed when performing synthesis in the KOH-DMSO environment. CsF was also used to increase the alkalinity of the medium. The essence of the high basicity property of the KOH-DMSO system is related to the strong solvation of cations and weak anions. It should also be taken into account that KOH is poorly soluble and has a low degree of dissociation in a mixture with dimethyl sulfoxide. This provides a basis for considering the changes that occur with non-dissociated alkali molecules along with the traditional anionic mechanism. Among the catalysts used in the experiment, the most effective was KOH, in which the yield of resorcinol in the mono - position of vinyl ether was 31,7%, and when using LiOH and NaOH – 14,6 and 22,7%, respectively.

Keywords: acetylene, vinyl acetylene, catalyst, resorcinol, KOH-DMSO, dimethylformamide, dimethylsulfoxide.

Introduction

Aromatic vinyl esters containing a vinyl group are characterized by their resistance to hydrolysis and a tendency to radical polymerization compared to aliphatic analogues. The reactivity of these substances as a building block in organic synthesis is very high [1, 2].

There are several schools of scientists whose research works are aimed at the synthesis of vinyl esters and the study of their derivatives. One of them is the scientific school of F. V. Kalabin. They used acetylene as a vinylating agent in their vinyl ether production technology. Arylvinyl esters synthesized by them are widely used in the synthesis of polymers, diene and polyenes, as well as in the synthesis of biologically active substances [3, 4, 5].

The last few decades show rapid development of the chemistry of synthesis of arylvinyl esters and their derivatives. They are used in the synthesis of new composite polymers, as well as in the synthesis of preparations for plant protection [5].

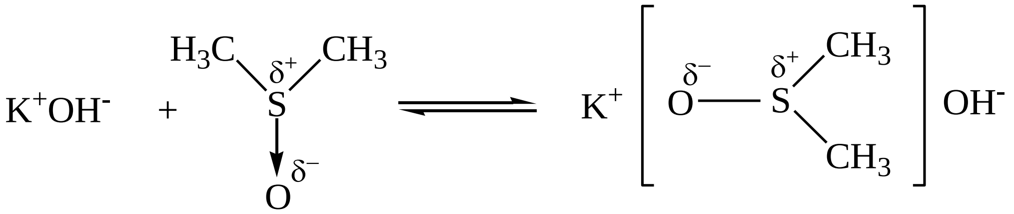
Acetylene due to the triple bond in its composition is one of the main raw materials in chemical synthesis. Thanks to these properties, it is possible to synthesize very important substances in the chemical industry, as well as in organic synthesis [6, 7].

To date, in the development of the fundamental basis of acetylene chemistry, the developments of A. E. Favorsky do not lose their significance. It is possible to perform the reaction of nucleophilic addition (vinylation) of acetylene in the form of an electrophile in a strongly alkaline medium and as a nucleophilic addition of acetylene with a carbonyl group C=O. Among super-modern environments, KOH/DMSO is one of the most stable, convenient and versatile systems [8-11].

Vinyl derivatives of aromatic hydrocarbons containing a hydroxo group are synthesized as heterocyclic compounds by vinylation with acetylene.

To date, the introduction of high-base systems consisting of a solution of alkaline-bipolar aproton into the chemistry of vinyl acetylene has allowed optimizing the conditions for obtaining difficult-to-synthesize vinyl compounds, as well as aromatic hydrocarbons and their vinyl esters.

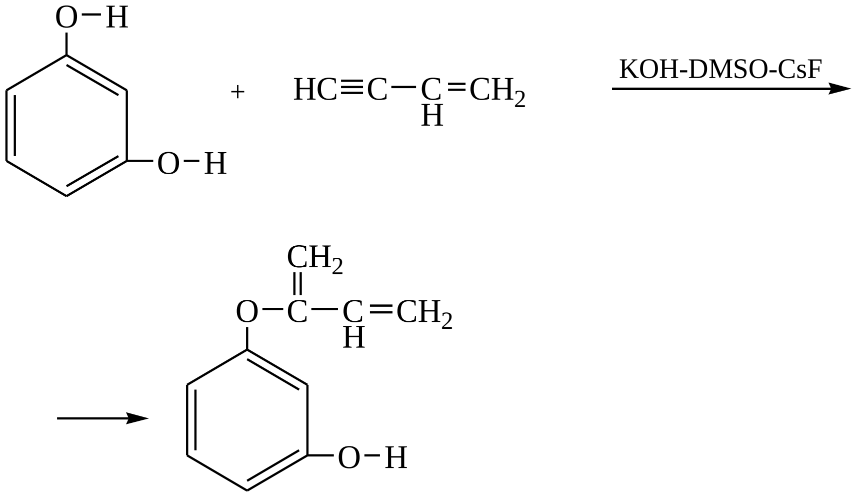
The study systematically studied the process of vinyl acetylene vinylation using high-base KOH-DMSO and KOH-DMFA systems in the presence of resorcinol (KOH) [12-16]. The role of DMSO in the KOH-DMSO system is that it causes dissociation of the base ion pair, as well as the formation of a high-base and low-solvatable dimsil anion:



It should be noted that the essence of this system should be explained in General by changes in the dielectric constant of the medium, hydrogen bonds, and other effects. If metal fluorides are added to the DMSO-KOH system, their basicity will increase, the process will be easier, and the yield of vinyl esters will be higher [17].

Material and methods

A CsF-mon-DMSO catalytic system with high basicity (M = Li, Na, K) was used for vinylation of resorcinol. In the process, the formation of resorcinol vinyl ether in the mono - position was determined, the schematic form of the reaction is as follows:



At the same time, the basicity of the system increases and allows you to dramatically increase the output of the resulting product.

Results

It is known that in many catalytic processes, the yield of the product and the direction of the reaction largely depend on the nature and quantity of the catalyst and solvent, temperature, molar ratios of the initial materials, as well as on the speed of introduction of the initial reagents.

The influence of the nature of the catalyst on the process of resorcinol vinylation is investigated. Lithium, sodium, and potassium hydroxides were used as catalysts. In all cases, resorcinol was found to form vinyl ether in the mono position. The results obtained in accordance with the nature of the catalyst used are shown in table 1.

Table 1

Catalyst	Yield, %
LiOH	14,6
NaOH	22,7
KOH	31,7

Influence of the nature of the catalyst on the yield of resorcinol vinyl esters in the mono-position (reaction time-3 hours, temperature-30°C)

According to the results, the relatively active catalyst was KOH, in which the yield of resorcinol vinyl ether in the mono position was 31,7%, using LiOH and NaOH-14,6 and 2,7%, respectively.

When conducting experiments without a solvent, the process of vinylation of resorcinol is difficult, because of the low yield of the product, it was impossible to separate it and determine its composition. The catalyst in the amount of 12-24% relative to the mass of resorcinol was tested for the vinylation process in the presence of DMSO.

The vinylation process was performed at atmospheric pressure in the presence of alkali metal hydroxides. It was found that the activity of catalysts decreases in the following order:

$$CsOH \cdot H_2O > KOH \cdot H_2O > NaOH \cdot H_2O > LiOH \cdot H_2O$$

Comparing the catalytic activity of KOH and $2KOH \bullet H_2O$, $KOH \bullet H_2O$, it was shown that the amount of water in all cases complicates the vinylation process. CsOH has been found to be relatively highly effective, where anhydrous alkali metal hydroxides are used in the vinylation process. However, dehydration of rubidium and caesium hydroxides is very difficult. It is usually boiled with solvents such as octane, toluene, and xylene, which form an azeotropic mixture with water and remove the water.

According to the results obtained in the experiment, the amount of KOH in the system has a significant effect on the course of the reaction, and its optimal amount was 13% by weight of resorcinol, in subsequent experiments, the amount of the catalyst was the above amount.

The effect of solvents on the resorcinol vinylation reaction was studied with a reaction time of 2,5 hours (table 2).

Table 2

№	Nature of the solvent	Temperature , °C	amount of catalyst KOH, % (relative to the mass of resorcinol)	The yield of vinyl ether of resorcinol mono - position, %
1.	-	25-30	13	5,2
2.	DMSO	25-30	13	20,3
3.	DMFA	25-30	13	16,3

Influence of the solvent on the process of resorcinol vinylation
(Reaction time-2,5 hours)

From the above data, it can be seen that the nature of the solvent significantly affects the vinylation reaction of resorcinol. During the formation of resorcinol vinyl ether in the mono position, the yield was 5.2% and under the same conditions with the participation of DMSO, the yield was 20,3%. To study the effect of the nature of the solvent on the reaction the process was performed in the presence of DMFA at 25-30°C with a catalyst content of 11% (relative to the mass of resorcinol). At the same time, the yield was 16,3%. Among the solvents used, DMSO was found to be more active than DMFA in the vinylation process. This is due to the fact that, as mentioned earlier, polar two-proton solvents form a highly alkaline system with KOH. This increases the basicity of KOH and accelerates the nucleophilic attachment of the intermediate compound-potassium resorcinate with vinyl acetylene.

Discussion. To further increase the yield of resorcinol vinyl ether in the mono position, the KOH-DMSO-CsF system was studied. The temperature was maintained in the range of 25-45 °C. The results are shown in table.3.

Table 3

№	Temperature, °C	Reaction time, hour	The yield of vinyl ether of resorcinol mono - position, %
1.	25-30	1	25,6
2.	25-30	2	28,5
3.	25-30	3	34,2
4.	25-30	4	35,3
5.	25-30	5	38,7
6.	30-35	5	50,2
7.	50-75	5	36,5

Temperature effect on the yield of resorcinol vinyl ether in the mono-position with the KOH-DMSO-CsF system (the amount of KOH catalyst relative to the mass of resorcinol is 13%)

The table shows that when the reaction time increases from 1 to 5 hours, the yield of resorcinol vinyl ether in the mono-position passes through the maximum. At a temperature of 25-30 ° C and a reaction time of 3 hours, the yield of the product is 34,2%. a Further increase in the reaction time leads to a decrease in the yield of resorcinol vinyl ether in the mono-position, its yield reaches the maximum value after 5 hours, i.e. 38,7%.

An increase in temperature to 30-35 °C led to an increase in product yield by 50,2%. An increase in temperature above 50°C led to a decrease in product yield. This can be explained by oligomerization of the synthesized vinyl compound and partial oxidation of resorcinol and the resulting product, or by a decrease in the solubility of vinyl acetylene at high temperatures and a destructive change in the product.

Thus, studies of the resorcinol vinylation reaction showed that the highest yield of the product (50,2%) and the optimal conditions for the process are: the solvent - DMSO, the amount of the catalyst KOH - 13% (relative to the mass of resorcinol), the temperature is 30-35 °C, and the reaction time is 5 hours.

Based on the results of the study of the influence of temperature on the course of the resorcinol vinylation reaction, a graph of the yield of resorcinol vinyl ether at different temperatures, depending on the duration of the reaction (Fig. 1).

According to the results of experiments, it was found that the temperature has a significant effect on the yield of the product. In all cases, the yield of the product increases depending on time and temperature. When the temperature is raised from 30 to 35 ° C with a reaction time of 5 hours, the yield of the product also increases from 38,7 to 50.2%, respectively. Further increase in temperature slows down and at 75 ° C the product yield is 36,5%.

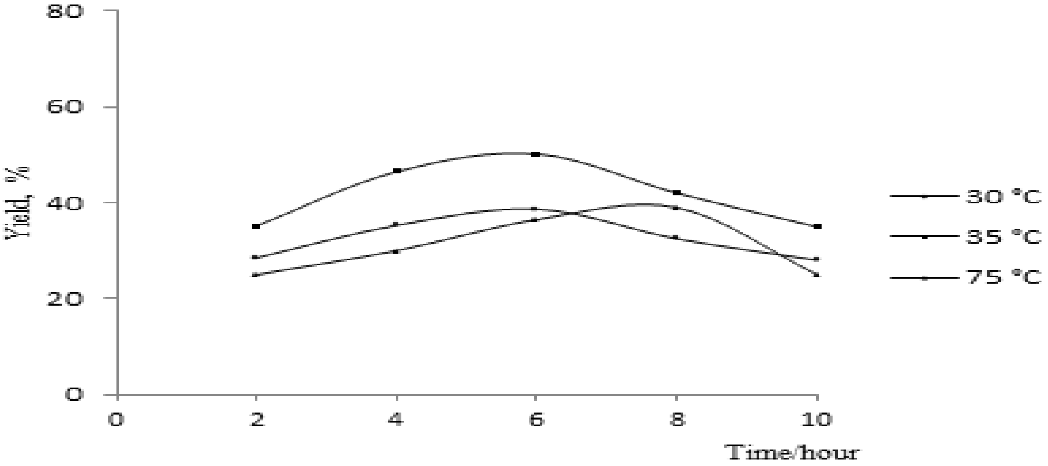


Fig. 1. Effect of the reaction duration at different temperatures on the yield of resorcinol vinyl ether in the mono-position.

Based on the data obtained, a graph of the temperature dependence of the product yield was drawn up (Fig. 2). This pattern is explained by a decrease in the solubility of vinyl acetylene at high temperatures, which leads to a decrease in its content in the reaction system, a decrease in the reaction rate and the yield of resorcinol vinyl ether in the mono-position.

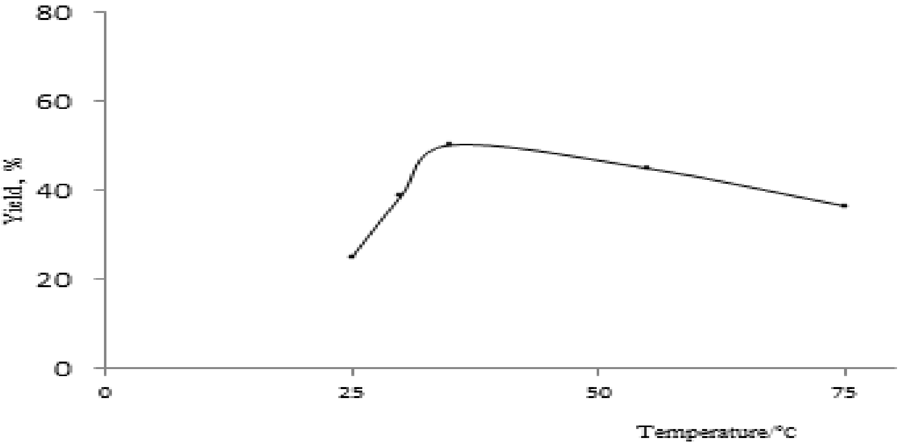


Fig. 2. Temperature dependence of resorcinol vinyl ether yield in mono-position (Reaction time 5 hours)

Conclusion

The influence of the catalyst, temperature, and solvent in the vinylation reaction based on vinyl acetylene was studied. Based on the results of the study, the vinylation reaction was performed in a super-new medium (KOH / DMSO). The higher activity of KOH in the reactions of vinylation of phenols with vinyl acetylene than LiOH and NaOH can be explained by the fact that easily forms the corresponding ethinides and phenolates.

The results of these studies can be applied to aromatic oxic acids, nitrogen and sulfur-containing heterocyclic compounds, alcohols, thiols and acetoxides in addition to phenols. Based on the results of the study, a method of homogeneous-catalytic vinylation of resorcinol with vinyl acetylene at atmospheric pressure was developed.

REFERENCES

[1] Trofimov, B.A., Oparina, L.A., Kolyvanov, N.A., Vysotskaya O.V., Gusarova N.K. Nucleophilic addition to acetylenes in superbasic catalytic systems: XVIII. Vinylation of phenols and naphthols with acetylene //Russian Journal of Organic Chemistry. – 2015. – T. 51. – №. 2. – C. 188-194.

[2] Ларионова Е.Ю., Кэмпф Н.В., Орел В.Б. Исследование процесса переноса протона в реакции винилирования метанола в среде КОН/ДМСО методами квантовой химии. Вестник ИрГТУ, 2011. - №4. – -С. 183-185.

[3] Трофимов Б.А. Суперосновные катализаторы и реагенты: концепция, применение, перспективы. Современные проблемы органической химии. – 2004. – Вып. 14. – С.

[4] Мирхамитова Д.Х., Нурманов С.Э., Хабиев Ф.М., Худайберганова С.З., Тешабаев Б. Разработка катализаторов для синтез N-винилморфолина. // II Межд. науч. конф. «Современная химия: Успехи и достижения». -Чита. -2016 г. -С. 282-283.

[5] Зиядуллаев О.Э., Мирхамитова Д.Х., Нурманов С.Э. Турли усуллар ёрдамида ароматик ацетилен спиртлари синтези. // ЎзМУ Хабарлари журнали. -Тошкент, -2012. -№3/1. -С.25-29.

[6] Мирхамитова Д.Х., Нурманов С.Э., Жураев В.Н. Каталитический синтез N-винилпиперидина. // Журн. ХПС. -Ташкент. -2001. -Спец. вып. -С.86-87.

[7] Мирхамитова Д.Х. Азот тутган гетероҳалқали бирикмаларни винилҳосилалари синтези ва хоссалари. // ЎзМУ Хабарлари журнали. -Ташкент, -2012. -№3/1. -С.79-84.

[8] Олимов Б.Б., Ахмедов В.Н. Винилацетилен асосида фенолларнинг винил эфирлари синтези. "Замонавий ишлаб чикаришнинг мухандислик ва технологик муаммоларини инновацион ечимлари" Халкаро илмий анжуман материаллари Бухоро. 2019. 37-39 б.

[9] Olimov B.B., Ahmedov V.N., Hayitov S. Ikki atomli fenollar asosida vinilli efirlarni olish usullari. Fan va texnologiyalar taraqqiyoti ilmiy – texnikaviy jurnal. - № 1/2020.

[10] Олимов Б.Б., Ахмедов В.Н., Назаров Ш.К. Электронная структура и квантово-химические расчёты виниловых эфиров фенолов. U55 Universum: химия и биология:

научный журнал. – № 4(70). М., Изд. «МЦНО», 2020. – 53-57с.

[11] Nazarov Sh.K., Olimov B.B., Akhmedov V.N. Electronic structure and quantum-chemical calculations of vinyl esters of phenols. Austrian Journal of Technical and Natural Sciences Scientifi journal № 3–4 2020 (March – April).

[12] Ахмедов В.Н., Олимов Б.Б. Винилацетилен асосида фенолларнинг винил эфирлари синтези. "Замонавий ишлаб чиқаришда муҳандислик ва технологик муаммоларнинг инновацион ечимлари" халқаро илмий анжуман материаллари. 3 ТОМ, 14-16 ноября 2019 г. Бухоро-2019.

[13] Ахмедов В.Н., Олимов Б.Б. Способ получения виниловых эфиров на основе винилацетилена. Dedicated to the 97 anniversary of the national leader of Azerbaijan, Heydar Aliyev IV international scientific conference of young researchers. Baku Engineering University, 2020 Baku/Azerbaijan

[14] Мирхамитова Д.Х., Нурманов С.Э., Тиллабаев А.А., Сирлибаев Т.С. Гомогенно-каталитический синтез N-виниланабазина. // журн. Вестник ГулГУ. -Гулистан. -2003. -№4. -С.86-88.

[15] Абдувалиева С., Нурманов С.Э., Мирхамитова Д.Х., Абдурасулов Б.Р. Юқори асосли системада бензотриазолни виниллаш. // "Биоорганик кимё фани муаммолари" Республика конференцияси. -Наманган. 21-22 ноябр 2014, -С.286-288.

[16] Mirkhamitova D.Kh., Nurmanov S.E., Khudayberganova S.Z., Yodgorova M. Catalytic vinylation of some heterocyclic amines at the atmospheric pressure. // Межд. конф. «Актуальные проблемы инновационных технологий в развитии химической нефтегазовой и пищевой промышленности». -Ташкент. 26 мая 2016 г. -С.84-85.

[17] Абдувалиева С.Б., Мирхамитова Д.Х., Нурманов С.Э. Бензотриазолни гомоген-каталитик виниллаш. // Материалы VIII Межд. научно-технической конф. "Актуальные проблемы химии и химической технологии", -Навои. 19-21 ноября 2015 г. -С.80.