

SHORT COMMUNICATION

SYNTHESIS OF ALLYL PHENYL ETHER AND CLAISEN REARRANGEMENT[♦]

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Abstract: It has been established the possibility for phenol allylation on natural zeolites and them analogs. Here is demonstrated the synthesis of allyl phenol, which has wide industrial applications. The offered method in comparison with the traditional methods has more advantages – higher selectivity, smaller material and power resources consumption. It has been obtained the mixture of allylating phenols (30%) in general with allyl phenyl ether (1) with 80% yields. At 600 K is obtained allylphenyl ether, at 700 K beginning the formation of allyl phenols, which is the result of direct C-allylation of the aromatic ring. It has been investigated the possibility of Claisen rearrangement in the same conditions. All of that are established by gas-liquid chromatography and liquid chromatography data.

Keywords: *allyl alcohol, allylation, Claisen rearrangement, natural zeolite, phenol*

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INTRODUCTION

In the processes of chemical technology, as a rule, there are a lot of stages and manufactures, which can be supplemented by various stages of recycling processes. Allyl phenols are raw material for the manufacture of a wide assortment of organic compounds, in producing of biologically active compounds, accelerators for rubber vulcanization, explosives, lubricant oils, gasoline anticorrosive additives, etc. Finding of new ways for synthesis and chemical transformation of allyl phenol, despite of rich history of researches, still presents scientific and applied interest.

EXPERIMENTAL

The synthesis of allyl phenyl ether is carried out by the interaction of allyl alcohol with phenol (molar ratio = 1:1) in the presence of zeolite and hydroquinone (0.5 g for 0.5 mol allyl alcohol). The allyl alcohol was brought in flask with the drained complex of phenol on zeolites. The temperature of reaction medium rose up to 250 - 300°C. The reaction products were removed by diethyl-ether and dried on MgSO₄. Reaction products were analyzed by chromatography.

Gas-liquid chromatography (GLC): with heat conductivity detector; columns: stainless steel 2 m × 3 mm; additionally: 7% silicon elastomer E-301 on chemosorb AW-HMDS (0.26 - 0.36 mm), 15% Carbovax 20M on Chromatone N-AW-HMDS (0.126 - 0.160 mm) and 5% E-30 on chromatone DMCS (0.400 - 0.630 mm); carrier gas: helium (flow: 30-60 mL/min); temperature of columns: 40 - 240°C.

The products are identified using thin layer chromatography (TLC) method as well. Silufol UV-254 plates are used. The eluent for TLC was C₆H₆ : EtOH (2:1 v/v) mixture. The spots are developed by iodine vapors.

The isolated products are identified by IR (Specord IR-75) and NMR (Varian "Mercury-300" RS) methods. The chemical shifts are expressed by ppm with respect to Si(CH₃)₄. The solvent was CDCl₃.

By vacuum distillation four fractions are isolated.

First fraction (87%): main product - allylphenyl ether (1); b.p. 75°C/15 mm; n_D²⁰ 1.5207/351/. IR spectrum: 699...760 (the monosubstituted benzene); 930...997 (CH=CH₂); 1220...1260 (C-O); 1500...1600 (C=C). NMR: 4.38 (2H, OCH₂, 4.8 I 1.4 Hz); 5.18÷5.29 m (2H, =CH₂); 5.92 (1H, CH, 17.0 and 10.0 Hz); 6.6÷7.3 m (5H, C₅H₆).

Second fraction (5%): a mix boiling at 89 - 94°C/15 mm; n_D²⁰ 1.5292. By comparison with known samples it was found, that the fraction consists of: of allyl phenyl ether (1) - 71%, the mixture of allyl phenols (4 and 5) 22%, and the mixture of allyl(*o*-allyl) phenyl ether (2) and allyl(*p*-allyl) phenyl ether (3) - 7%.

Third fraction (5%): here is a mix with boiling temperature 110 - 114°C/15 mm; n_D²⁰ 1.5264. By comparison with known samples it is found that the fraction consists of allylphenyl ether (1) 45%, the mixture of allyl phenols (4 and 5) 43%, the mixture of allyl(*o*-allyl) phenyl ether (2) and allyl(*p*-allyl) phenyl ether (3) 12%.

Fourth fraction (3%): a mix boiling at 116 - 118°C/15 mm; n_D²⁰ 1.5364. By GLC it is found that the fraction consists from the mixture of allylphenols (4 and 5) - 45%, the mixture of allyl(*o*-allyl) phenyl ether (2) and allyl(*p*-allyl) phenyl ether (2 and 3) - 55%.

Individual reaction products are allocated by liquid chromatography of a crude reactionary mix of similarly spent experience, after distillation of volatile products. A column with internal diameter 1.5 mm, filled with 45 g of silica (eluent volume 600 mL, speed of 1 mL/min) is used. Division is supervised by GLC and TLC.

RESULTS AND DISCUSSION

Earlier it has been investigated the alkylation of phenol by allyl bromide for the purpose of selective synthesis of allyl phenyl ether in phase transfer catalysis (PTC) conditions [1].

It has been established, that phase transfer catalysis system catalyzed phenol allylation. Depending on reaction conditions along with wanted allyl phenyl ether (1) turns out also allyl (*o*-allyl) phenyl ether (2), allyl (*p*-allyl) phenyl ether (3), and also insignificant quantities of diallyl ether (owing to hydrolysis of allyl bromide to allylic alcohol and further its alkylation formed) and also (*o*-allyl) phenol (4) and (*p*-allyl) phenol (5) (Figure 1).

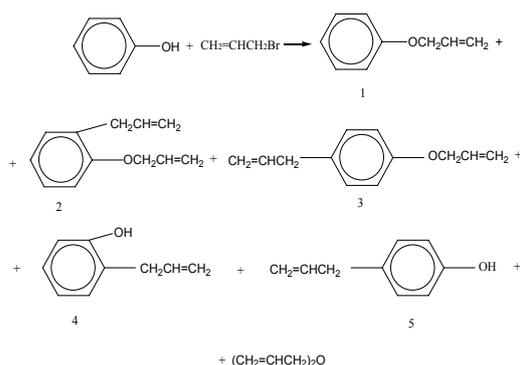


Figure 1. Reaction products from the alkylation of phenol with allyl bromide

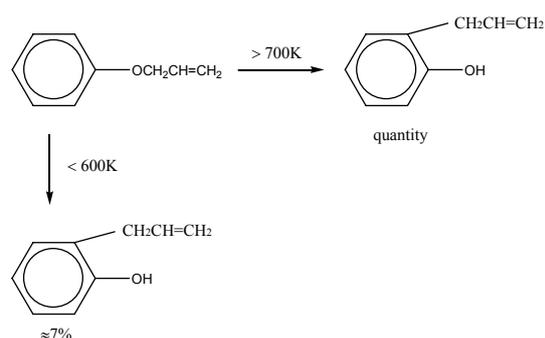


Figure 2. Claisen rearrangement yield as a function of temperature

In the presence of PTC catalysts carrying over quantities allylphenyl ether (1) from 11.6% without the catalyst to 55.8% with the catalyst (SAC as catamine AB) increase. It has been established also, that in the system “solid phase-liquid”, especially with the dehydrated powder of potassium hydroxide in toluene it is formed exclusively allyl phenyl ether. It was co-ordinated with those circumstances that hydrate forms a cover around phenolate anion, stirs *o*-alkylation, promoting joining a fragment of carbon on benzene rings. It is experimentally proved, that formation of allylphenols (4 and 5) is a consequence of direct carbon alkylation of phenolate anion, instead of the result of the Claisen rearrangement of allyl phenyl ether.

The present work is aimed to develop a method for allylation of phenol on Armenian natural zeolites as catalysts. A natural zeolite – clinoptilolite & mordenite produced in Armenia was employed for this study [2]. Armenian clinoptilolite and its modified analogs are high silica and they have been used in some organic compounds (aniline, phenol, benzene, toluene, xylene) sorption processes [3].

In our opinion, the allylation of phenol on the same catalytic system can give a possibility to specify the mechanism offered by us, that the transformation of allyl alcohol to aromatics proceeds depending on the pore size of zeolites [2, 3]. It has been obtained a mixture of allylating phenols (around 30% at the using phenol) in general with allyl phenyl ether (**1**) with 80% yields.

It is known, that at temperatures lower than 600 K, the surface of zeolite becomes covered by phenol, and phenol forms the complex with a surface. The phenol molecule rather on surface, possibly, settles down so, that phenol group remains free. For example, the methylation by methyl alcohol in mentioned temperatures goes only on heteroatom, with formation of anisol. In our case also allylation passes thus with the formation of allyl phenyl ether mainly. The allylation to a ring is possible only on a free surface, possibly, through direct allylation with allyl radicals. Given established also that fact, that a product of Claisen rearrangement with the formation of allyl phenol (**4** and **5**) is happening at temperatures above 400°C (Figure 2).

The heating of allylphenol ether (**1**) in alkylation reaction conditions leads to the formation of *o*-allylphenol (**4**) or *p*-allylphenol (**5**), with a low output. The output of C-allylated phenol products is increased at higher temperatures.

On the basis of these assumptions it is possible to affirm that at lower temperatures C-alkylation takes place in nucleus.

CONCLUSIONS

It has been established that Armenian zeolite can be used as catalyst for phenol allylation process. The present research shows an opportunity of using phenol adsorbed on zeolite. This task is also the way of recycling the zeolite and the harmful waste such as phenol.

ACKNOWLEDGEMENTS

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