

SYNTHESIS AND STUDY OF ANTIOXIDATIVE PROPERTIES OF AMINOMETHYLATED DERIVATIVES OF *p*-(CYCLOHEXENE3-YL-ETHYLPHENOL)

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Received 24.05.2018

Abstract: The paper deals with the results of research into phenol cycloalkenylation with 3-vinylcyclohexene in the presence of modified zeolite-containing catalyst Zeokar-2M on the laboratory batch unit and aminomethylation of the obtained *p*-(cyclohexene-3-yl-ethyl) phenol with formaldehyde and aniline. The temperature effects, reaction time, molar ratio of phenol to vinylcyclohexene (VCH) and amount of the catalyst on the yield and selectivity of phenol cycloalkenylation with VCH were studied to define optimal conditions that ensure the maximum yield of the target product. The obtained products were tested as antioxidants for diesel fuel and showed satisfactory results, which indicates the effectiveness of their use.

Keywords: phenol, 3-vinylcyclohexene, catalyst, cycloalkenylation, aniline, aminomethylation, antioxidants

Introduction

Among a large number of petrochemical products, alkylphenols are widely used as initial reagents in the synthesis of fuel additives and stabilizers, inhibitors of free-radical oxidation of organic and bioorganic substrates, herbicides, fragrances, etc. [1-6].

The use of antioxidants is economically advantageous, so their production in technologically advanced countries is ahead of other chemical production [7-11].

The purpose of the work is to study cycloalkenylation process of phenol 3-vinylcyclohexene (VCH) using a modified zeolite-containing catalyst Zeokar-2M in a batch plant; subsequent interaction of the obtained *p*-(cyclohexen-3-yl-ethyl)-phenol with formaldehyde and anilines; synthesis of 2-hydroxy-5(cyclohexen-3-yl-ethyl) benzylphenylamines (BPhA) and testing them as antioxidants for diesel fuel.

Experimental Part

2-Hydroxy-5(cyclohexene-3-yl-ethyl)-benzylphenylamines was obtained in two stages on a batch unit:

The I stage – phenol cycloalkenylation reaction with 3-vinylcyclohexene.

Phenol and 3-vinylcyclohexene were used as feedstock and modified zeolite-containing Zeokar-2M (TU 38-101483-77) as a catalyst for the reaction. Phenol was used in a chemically pure, freshly distilled form.

VCH was obtained by cyclodimerization of divinyl [12] followed by allocation of a close-cut fraction through precision fractional distillation on a column. Note that 3-vinylcyclohexene with a purity of 98.8 - 99.0% was taken for the cycloalkenylation reaction with boiling point of 130 °C, $\eta_D^{20} = 1.4648$, $\rho_4^{20} = 0.8308$, and a molar mass of 108.

Phenol cycloalkenylation with VCH was carried out in a three-neck flask. The resulting alkylate was exposed to rectification at the end of the reaction. In the course of rectification, at first, non-reacting VCH and phenol (to 200° C) were distilled off under atmospheric pressure

followed by allocation of the target product under low pressure (1333 Pa) and determination of its purity and physical-chemical properties. The structure and composition of the products were determined through the use of spectral methods and chromatographic analysis.

The II stage – aminomethylation reaction of p-(cyclohexene-3-yl-ethyl)-phenol with formalin and aniline (2,6-diisopropylaniline).

Note that p-(cyclohexen-3-yl-ethyl)-phenol, formalin, aniline and 2,6 diisopropylaniline were used as feedstock. Also, aniline and 2,6-diisopropylaniline were used in a chemically pure form with the following properties: aniline – $T_b = 184\text{ }^\circ\text{C}$, $\eta_D^{20} = 1.5863$, $\rho_4^{20} = 1.0217$, molecular mass = 93; 2,6-diisopropylaniline – $T_b = 254\text{--}257\text{ }^\circ\text{C}$, $\eta_D^{20} = 1.5330$, $\rho_4^{20} = 0.9400$, molecular mass = 177.

Besides, 2-Hydroxy-5-alkylbenzylphenylamine was obtained by interaction of para-alkylphenol with formaldehyde and aniline (or 2,6-diisopropylaniline) in the ratio of 1:2:2.

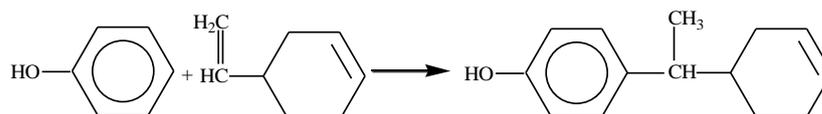
Also, p-Alkylphenol, aniline (or 2,6-diisopropylaniline) and benzene were put into a three-necked flask equipped with a mechanical stirrer and a thermometer. While stirring, formaldehyde solution of 30% was drop wisely added to the reaction mixture at a temperature of $30\text{ }^\circ\text{C}$ and then it was kept for 1 h. It was followed by gradual rise in a temperature up to $80\text{ }^\circ\text{C}$ and keeping it for another 2 h by permanent stirring and washing with water to remove non-reacting formaldehyde.

Amino compounds were purified from alkylphenol through their transfer into hydrochloric acid salt. Further, aqueous solution of amine hydrochloric acid salt was treated by a concentrated solution of NH_4OH while free amine compounds were allocated. The resulting amine was separated from water by extraction with benzene, and then exposed to rectification under vacuum.

After isolating the target product, its physical-chemical properties were determined and structural formula confirmed.

Results and its Dscussions

The I stage – Phenol interaction with VCH in the presence of a catalyst results in formation of p-substituted phenol is as follows:



To find out optimal conditions, ensure maximum yield and identify composition of the reaction product of p-(cyclohexenethyl) phenol, there were studied effects of the temperature, the time and the molar ratio of phenol to VCH, as well as the catalyst amount.

The reaction temperature varied in the range of $90\text{--}130\text{ }^\circ\text{C}$, the reaction time – 1-5h, the molar ratio of phenol to VCH – from 1:2 to 2:1 mol/mol, and finally the catalyst amount – 5-25%.

The results of phenol cycloalkenylation reaction with 3-vinylcyclohexene in the presence of Zeokar-2M catalyst are presented in Fig. 1.

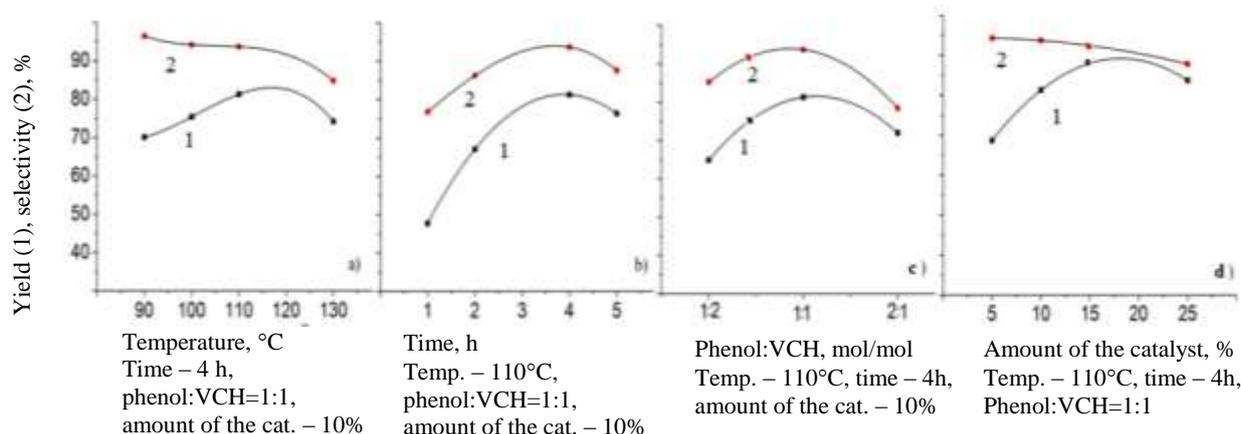


Fig.1. Dependence of the yield (1) and selectivity (2) of p-(cyclohexene-3-yl-ethyl)phenol on temperature, time, molar ratio of the initial components and the catalyst amount.

As is evident from Fig.1, the highest yield of the target product – 81.3% is achieved on the phenol from theory, but selectivity – 93.7% (for the target product) at temperature of 110 °C. The yield of p-(cyclohexenyl) phenol decreases to 74.3%, and the selectivity to 85.5% through raising the reaction temperature up to 130 °C. The maximum yield of the target product is observed in 4 h lasting reaction.

As is seen from Fig. 1 (c), to increase the VCH conversion it is necessary to rely on the ratio of 1:1 mol/mol for phenol:VCH. The yield of the target product rises by nearly 2-3% in the mixture of initial components through increasing the VCH concentration; however, in this case the selectivity of the process reduces. This is explained as being due to the increase of the concentration of other isomers in alkylate. The data obtained through the study into the catalyst amount is of great interest. As is seen from the Fig., the yield of the target product amounts to 81.3%; however, the selectivity is 93.7% according to the target product in 10% of the catalyst amount.

Thus, optimal conditions for carrying out phenol cycloalkenylation reaction with VCH in the presence of modified catalyst Zeokar-2M are as follows: temperature of 110°C, reaction time 4 h, molar ratio of phenol to 3-vinylcyclohexene 1:1 mol/mol, catalyst amount – 10% in the phenol used. In these conditions the yield of p-(cyclohexene-3-yl-ethyl) phenol amounts to 81.3% in the phenol used as per the theory; however, the selectivity is 93.7% on the target product.

All of the allocated reaction products are specified; physical-chemical properties determined and structural formula confirmed.

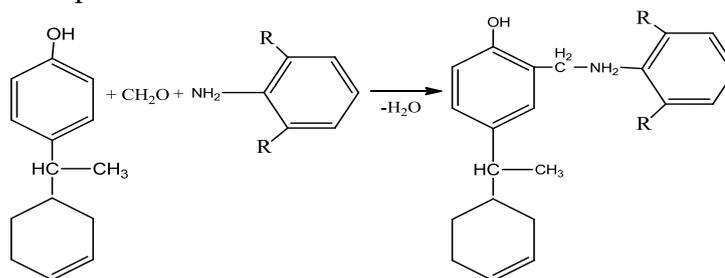
It should be added that identification of synthesized p-(cyclohexenylethyl) phenol was carried by ¹H NMR and IR-spectroscopies. In ¹H NMR spectrum of p-(cyclohexen-3-yl-ethyl) phenol has a singlet CH₃ -group of 1.20 ppm region, a multiplet with a large peak ($\delta = 1.77$ ppm), a singlet of 1.5 ppm which are characteristic for protons of CH₂-, CH-hydrocarbon ring, a singlet in the region of the OH-group 5-6 ppm, shifting into a strong field by dilution and a multiplet of 1,4-substituted-benzene ring corresponding approximately to the spectrum of AB type with an average chemical shift of 6.87 ppm and constant of $\nu = 8.5 \pm 0.5$ Hz.

It is important to note that IR absorption spectrum of p-(cyclohexenylethyl) phenol contains bands within the range of 1505, 1592-1610 cm⁻¹ (benzene ring), 3010, 3030 cm⁻¹ (stretching vibrations = CH₂), and OH group is determined by a band at 1240 cm⁻¹ and in the region of 3100-3500 cm⁻¹. Cyclohexene ring was confirmed by the C-H valence bands at 2920 and 2845 cm⁻¹, as well as by bands at 1108, 1345 cm⁻¹, characterizing δ_{CH_2} in the cycle. The methyl group is characterized by deformational vibrations at 1370 and 1460 cm⁻¹.

Table 1. Physical-chemical properties of p(cyclohexen-3-yl-ethyl)phenol

Structural formula	Boiling point at 5 mm Hg, °C	n_D^{20}	ρ_4^{40}	Mol. mass		Elemental composition, %			
				calc.	found	calc.		found	
						C	H	C	H
	147-148	1.5445	1.0040	202	202	83.2	8.9	83.9	9.4

The II stage – Aminomethylation process was carried out on a lab batch unit in liquid phase under atmospheric pressure.



where R = -H; -C₃H₇

73.4 g of 2-mono-substituted BPhA-1 was obtained containing 96.0% of the target product yield on p-alkylphenol taken from the theory.

Also, ¹H NMR spectrum of 2-hydroxy-5-(cyclohexen-3-yl-ethyl) benzylphenylamine contains protons of aromatic core (in the interval $\delta = 6.6$ -7.6 ppm), and a proton of hydroxyl (in regions $\delta = 6.4$ ppm).

Resonance signals of $\delta = 3.3$ -3.7 ppm correspond to the protons of NH-group. A proton signal of CH₂-group attached to the aromatic ring is observed in $\delta = 5.15$ ppm region, and the singlet of CH₃-group is observed in 1.20 ppm region; CH₂-, CH-protons of cyclohexene ring are observed as a large multiplet peak in the region of $\delta = 1.5$ -1.7 ppm.

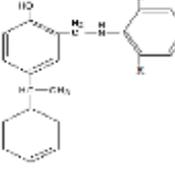
Besides, a benzene ring in IR spectrum of 2-hydroxy-5(cyclohexen-3-yl-ethyl) benzylphenylamine is observed in the regions of 2505, 1590-1608cm⁻¹; stretching vibrations = CH – in the regions of 3008, 3026 cm⁻¹, a hydroxyl group – in the region of 1240 and 3100-3505 cm⁻¹. C-H stretching vibrations of C-H cyclohexene ring is observed in the region of 2920-2840 cm⁻¹, stretching vibrations of CH₂ in the cycle is determined in the region of 1110 and 1345 cm⁻¹; CH₃-group is observed in the region of 1370- and 1460 cm⁻¹, and -NH-group – in the region of 1527 cm⁻¹.

By the same procedure, aminomethylation reaction of p-(cyclohexen-3-yl-ethyl) phenol was carried out with formaldehyde and 2,6-diisopropylanilin. The yield of 2-hydroxy-5(cyclohexen-3-yl-ethyl) benzyl-2,6-diisopropylphenylamine (BPhA-II) was 82.3%.

After purification from other admixtures, physical-chemical properties were determined and chemical structures confirmed. The IR and ¹H NMR spectra of BPhA-II are similar to the first amine.

Physical-chemical properties of 2-hydroxy-5(cyclohexen-3-yl-ethyl) benzylphenylamines are shown in Tab. 2.

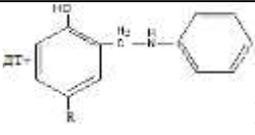
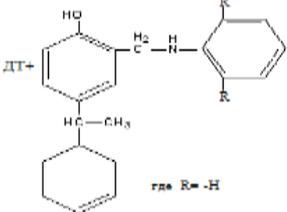
Table 2. Physical chemical properties of 2-hydroxy-5-(cyclohexen-3-yl-ethyl) benzylphenylamines

	Boiling point at 10 mm Hg, °C	n_D^{20}	ρ_4^{40}	Mol. mass	Elemental composition, %			
					calc.		found	
					C	H	C	H
R = -H	216-218	1.5810	0.9815	307	82.1	8.1	81.7	7.7
R = -C ₃ H ₇	224-228	1.5963	0.9875	391	82.9	9.5	82.3	9.2

2-Hydroxy-5-(cyclohexen-3-yl-ethyl) benzylphenylamines were tested as antioxidants of diesel fuel on GOST 9144-79. The samples were prepared on the basis of the known compositions (0.004%) and synthesized by us, too. Further, initial diesel fuel (DF) and samples with added antioxidants were oxidized on LSART device at 150°C during 4 h and the resulting residues determined.

The test results are shown in Tab. 3.

Table 3. Comparative test results of 2-hydroxy-5-(cyclohexen-3-yl-ethyl) benzylphenylamines as antioxidant (AO) of diesel fuel

No.	Antioxidants	Antioxidant amount, %	Sediment amount, mg/100 cm ³
1.	DF (without AO)	-	4.35
2.	DF+ ionol	0.004	1.0
3.	 R- polymerdistillate (known)	0.004	0.9
4.	 where R = -H	0.004	0.5
5.	R = -C ₃ H ₇	0.004	0

As is evident from Tab. 3, addition of aniline-based compound we synthesized causes the formation of insignificant sediment (0.5 mg/100 cm³) in DF; however, any sediment is formed by adding an antioxidant on the basis of 2,6-diisopropylaniline.

Conclusions

- Cycloalkenylation of phenol with 3-vinylcyclohexene has been studied in the presence of modified zeolite-containing catalyst Zeokar-2M. It revealed that at a temperature of 110°C, reaction time of 4 h, 1:1 molar ratio of phenol to VCH and catalyst amount of 10%, the yield of p-alkylphenol amounts to 81.3% on phenol according to the theory; however with selectivity – 93.7% on the target product.
- Aminomethylation reaction of p-alkylphenol with formalin and aniline has been studied. As a result, it found that at a temperature of 80 °C, reaction time of 2 h, 1:2:2 molar ratio of p-alkylphenol to formalin and aniline, the yield of 2-hydroxy-5-alkylbenzylphenylamines amounts to 82.3-96.0% according to the theory.

3. Synthesized 2-hydroxy-5(cyclohexen-3-yl-ethyl) benzylphenylamines have been tested as antioxidants for diesel fuel to meet results required.

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СИНТЕЗ И ИССЛЕДОВАНИЕ АНТИОКИСЛИТЕЛЬНЫХ СВОЙСТВ АМИНОМЕТИЛИРОВАННЫХ ПРОИЗВОДНЫХ *p*-(ЦИКЛОГЕКСЕН-3-ИЛ- ЭТИЛ)ФЕНОЛА

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*Исследованы реакции циклоалкенилирования фенола 3-винилциклогексеном в присутствии модифицированного цеолитсодержащего катализатора Цеокар-2М, на лабораторной установке периодического действия и аминометилирования полученного *p*-(циклогексен-3-ил-этил)фенола формальдегидом и анилинами. Изучено влияние температуры, продолжительности реакции, мольного соотношения фенол:винилциклогексен (ВЦГ) и количества катализатора на выход и селективность процесса циклоалкенилирования фенола винилциклогексеном, в результате чего найдены оптимальные условия, обеспечивающие максимальный выход целевого продукта. Полученные продукты были испытаны в качестве антиоксидантов к дизельному топливу и показали удовлетворительные результаты, что свидетельствует об эффективности их применения.*

Ключевые слова: фенол, 3-винилциклогексен, катализатор, циклоалкенилирование, анилин, аминометилирование, антиоксиданты

***p*-(TSİKLOHEKSEN-3-İL-ETİL)FENOLUN AMİNOMETİLLƏŞMİŞ TÖRƏMƏLƏRİNİN SİNTEZİ VƏ ANTIOKSİDLƏŞDİRİCİ XASSƏLƏRİNİN TƏDQIQI**

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*Fenolun modifikasiya olunmuş seolit tərkibli Seokar-2M katalizatoru iştirakında 3-vinilsikloheksenlə fasiləli laboratoriya qurğusunda tsikloalkenilləşmə və alınmış *p*-(tsikloheksen-3-il-etil)fenolun formaldehid və anilinlə aminometilləşmə reaksiyaları tədqiq olunmuşdur. Fenolun vinilsikloheksenlə tsikloalkenilləşmə prosesinin çıxımına və seçiciliyinə temperaturun, reaksiya müddətinin, fenolun vinilsikloheksenə mol nisbətinin və katalizatorun miqdarının təsiri öyrənilmişdir, nəticədə məqsədli məhsulun maksimum çıxımını təmin edən optimal şərait tapılmışdır. Alınmış məhsulların dizel yanacağına antioksidant kimi sınaqları aparılmış və qənaətbəxş nəticələr əldə olunmuşdur.*

Açar sözlər: fenol, 3-vinilsikloheksen, katalizator, tsikloalkenilləşmə, anilin, aminometilləşmə, antioksidant