



Synthesis of *p*-(Cyclohexene-3-yl-ethyl)phenol and Characteristics of its Phosphatization with Phosphorous Trichloride

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Cycloalkenylation of phenol with 4-vinylcyclohexene was studied in the presence of zeolite-Y catalyst, saturated by orthophosphoric acid on the batch unit. Phenol and 4-vinylcyclohexene were used as initial products for the realization of cycloalkenylation reaction. Cyclo-dimerization is realized in liquid phase in the presence of copper on zeolite as a catalyst, which has high selectivity according to buta-1,3-diene. All the separated products of reaction were characterized and their physico-chemical properties were determined. Chromatographic analysis was identified on chromatographer LKhM-72 with thermal conductivity detector. Synthesized *p*-(cyclohexenylethyl)phenol was identified by NMR and IR techniques. It is evident that the yield of target product *p*-(cyclohexenylethyl)phenol at optimum regime amounts to 72.4 % on theoretically, but selectivity found to be 97.7 % according to the target product. Tri-[*p*-(cyclohexenylethyl)phenyl] phosphite was obtained by the interaction of *p*-(cyclohexenylethyl)phenol with phosphorus trichloride and tested as an antioxidant for turbine oil T-46.

Keywords: Cycloalkenylation, Phosphorous trichloride, Zeolite-Y catalyst, Antioxidants.

INTRODUCTION

The alkylation of phenols is highly significant by technical point of view, as alkylphenols are widely applied in various fields as intermediate products for the synthesis of antioxidants, additives, plasticizers and other chemical additives to polyolefins, synthetic rubbers, oils and fuels [1-9].

Phenolic alkylation in acidic medium is one of typical reactions of electrophilic substitution and practically firstly alkylating agent is directed to *p*-position. Increasing the production of alkylphenols requires deep analysis and development of effective technology for the synthesis of alkylphenols, particularly cycloalkenylation process of phenol with 4-vinylcyclohexene (VCH) with application of Zeolite-Y as a catalyst, saturated by orthophosphoric acid on the batch unit, obtaining tri[*p*-(cyclohexenylethyl)phenyl]phosphite and its testing as an antioxidant for turbine oil T-46 [9-12].

EXPERIMENTAL

Phenol and 4-vinylcyclohexene were used as initial products for realization of cycloalkenylation reaction. Phenol was used as reactive agent and distilled before the experimental work. 4-Vinylcyclohexene was obtained by butadiene cyclodimerization. Cyclodimerization was carried out in liquid phase in

the presence of copper on zeolite as a catalyst of high selectivity according to buta-1,3-diene (more than 99 %), $T_{\text{boil.}} 130^{\circ}\text{C}$, $n_D^{20} 1.4648$, $\rho_4^{20} 0.8308$, m.w. 108.

The catalyst using orthophosphoric acid was developed by mixing thoroughly alumogel with cracking catalyst (zeolite type Y, $\text{SiO}_2:\text{Al}_2\text{O}_3 = 4.8$; ion-exchange degree: 97 %) was used for cycloalkenylation reaction of phenol with 4-vinylcyclohexene. The resulting mass was molded, pressed through a spinneret (1.6 mm in diameter), granulated and calcined. The catalyst was then impregnated with 10 % orthophosphoric acid solution (in terms of P_2O_5), evaporated, dried in an oven at 100°C and calcined at continuously increasing temperature from 200 to 600°C . Cycloalkenylation of phenol with 4-vinylcyclohexene was carried out on laboratory batch unit. The scheme of laboratory batch unit is shown in Fig. 1.

Phenol (1) and 4-vinylcyclohexene (2) in a certain ratio put into the mixer (3) from the container. Temperature is maintained at 45°C in phenol container. After mixing by the pump (4), they were transferred into the reactor (5). The component mixture, after passing through the catalyst bed enters to the top part of the reactor, where alkylate is collected in the container (7) after cooling and hereafter is directed rectification. The alkylate is transferred to Claisen's flask and rectified.

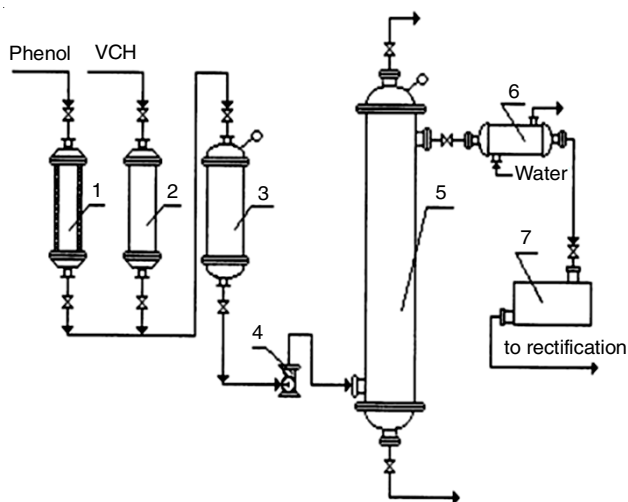


Fig. 1. Principal scheme of catalytic cycloalkenylation of phenol with 4-vinylcyclohexene; 1 – container for phenol; 2 – container for 4-vinylcyclohexene; 3 – mixer; 4 – pump; 5 – reactor; 6 – refrigerator; 7 – container for alkylate

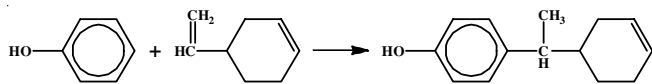
During rectification, unreacted 4-vinylcyclohexene and phenol (to 200 °C) were firstly distilled under atmospheric pressure and then the target product was separated under vacuum (5 mm Hg) and determined its purity and physico-chemical properties. The structures and contents of the products were confirmed with the help of spectral methods and chromatographic analysis.

Chromatographic analysis was carried out on LKhM-72 chromatograph with a thermal conductivity detector. The length of the column is 2 m, the solid carrier is chromate N-AW-DMC, washed with acid and silanized by dimethylchlorosilane, fraction 0.2 ± 0.25 mm. The fixed phase is SE-30 - methylsiloxane elastomer of 5 %. The initial temperature of the column is 50 and the final temperature ~ 280 °C, programming speed: 10 °C/min, velocity of helium carrier: 50 mL/min, evaporator temperature: 355 °C and the detector is 300 °C, the speed of the diagram tape is 60 mm/h. The internal normalization method based on the reduction of sum of peak areas to 100 % was used for the calculation.

IR-spectra were taken on “Specord M-80” spectrometer. NMR spectra were identified on Fourier spectrometer of “Bruker” company (Germany) at 300 MHz operating frequency at ambient temperature. Deuterated acetone was applied as solvent.

RESULTS AND DISCUSSION

Interaction of phenol with 4-vinylcyclohexene in the presence of phosphorus containing zeolite as catalyst proceeds with the formation of *p*-substituted phenol:

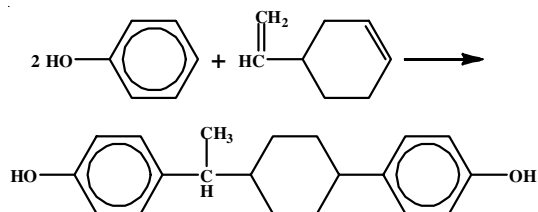


Interaction of temperature, molar ratio of phenol to 4-vinylcyclohexene and rate of volume flow on the yield and composition of the reaction product were studied for the purpose of determining of optimum conditions providing maximum yield of *p*-cyclohexenylethyl phenol.

The reaction temperature was changed in the range of 60–120 °C, molar ratio of phenol to 4-vinylcyclohexene was taken as 0.5–1:3 mol/mol and rate of volume flow from 0.2 to 1 h⁻¹.

The reaction results of cycloalkenylation of phenol with 4-vinylcyclohexene in the presence of catalyst are given in Table-1. From the data, it is evident that maximum yield of the target product 72.4 % is achieved at 110 °C. The yield of *p*-cyclohexenyl phenol decreases to 60.1 %, but selectivity to 89.4 % by increasing the temperature upto 120 °C. As can be seen from the data, it is important to consider phenol ratio to 4-vinylcyclohexene as 1:1 for increasing 4-vinylcyclohexene conversion. By increasing 4-vinylcyclohexene conversion in the mixture of initial components, the yield of the target product increases about 2–3 %, but simultaneously decreases the process selectivity. It occurs as result of increasing of concentration of other isomers in alkylate. 2-Mono, 2,4-, 2,6-di and 2,4,6-trisubstituted cyclohexenyl phenols were separated from the products of cycloalkenylation reaction of phenol with 4-vinylcyclohexene (Fig. 2).

Cyclobisphenol formation was also observed in the mixture of initial components by increasing of phenol concentration.



The data obtained by studying of the rate of volume flow, supply of the mixture of initial components are of interest. The yield of *p*-(cyclohexenylethyl)phenol amounts to 72.4 %, but selectivity 97.7 % (Table-1) on the target products at volumetric rate of 0.5 h⁻¹.

So, for proceeding of cycloalkenylation reaction of phenol with 4-vinylcyclohexene in the presence of phosphorus-containing catalyst zeolite-Y, at optimum regime *e.g.*, temperature of 110 °C, molar ratio of phenol to 4-vinylcyclohexene as 1:1 mol/mol and rate of volume flow 0.5 h⁻¹. All the separated reaction products were characterized and their physico-chemical properties and structural formulae were determined and confirmed.

Characterization of synthesized *p*-(cyclohexenylethyl)phenol was carried out by PMR and IR spectroscopies. singlet in CH₃-group in the field of 1.20 ppm, multiplet of a large peak ($\delta = 1.77$ ppm) 1.5 ppm characterizing for the protons of CH₂-, CH-hydrocarbon rings, singlet in OH- group of 5–6 ppm, shifted by dilution to a strong field and a multiplet of 1,4-substituted benzene ring corresponding approximately to the spectrum of species AB with an average chemical shift of 6.87 ppm and a constant ν equal to 8.5 ± 0.5 Hz are observed on PMR-spectrum of *p*-(cyclohexenylethyl)phenol.

IR spectrum of adsorption of *p*-(cyclohexenylethyl)phenol has the bands in the range of 1610–1592, 1505 cm⁻¹ (benzene ring), 3030, 3010 cm⁻¹ (valence vibrations =CH₂), OH-groups are determined according to the band at 1240 cm⁻¹ and in the field of 3500–3100 cm⁻¹. *gem*-Substituted cyclohexene ring was confirmed by the bands of C-H valence at

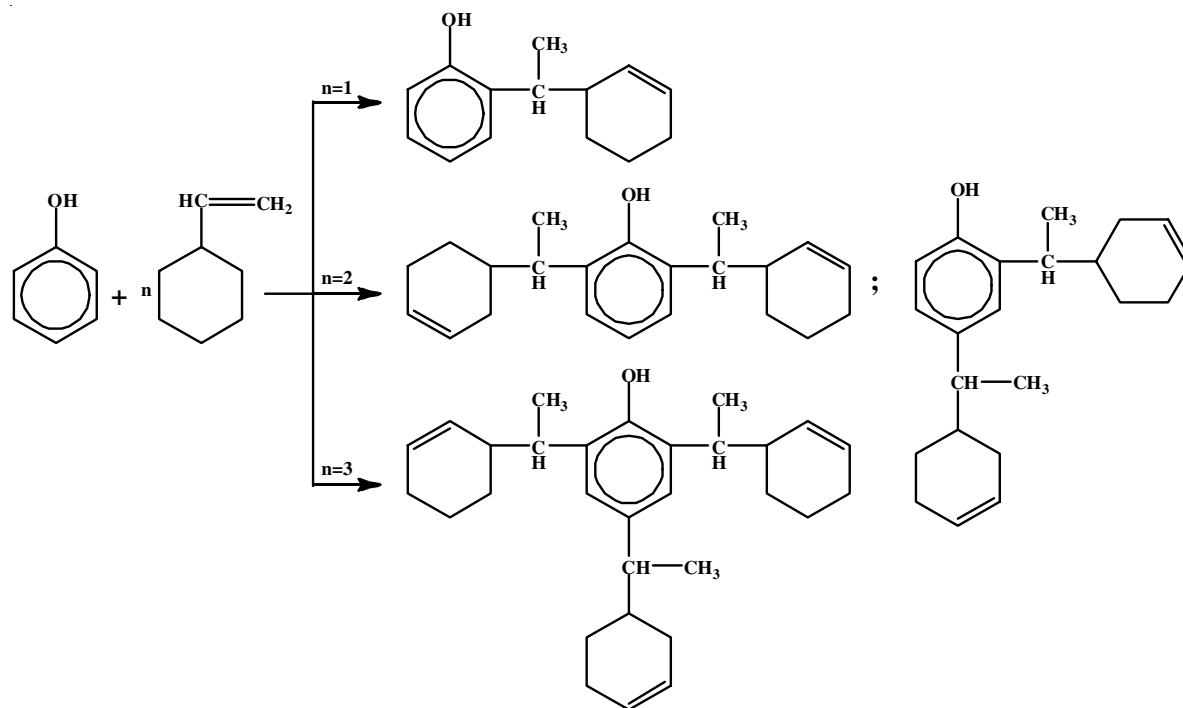


Fig. 2. Cycloalkenylation of phenol with 4-vinylcyclohexene at different concentrations

TABLE-1
RESULTS OF CYCLOALKENYLATION REACTION OF PHENOL WITH 3-VINYLCYCLOHEXENE IN THE PRESENCE OF ZEOLITE-Y CATALYST, SATURATED BY ORTHOPHOSPHORIC ACID ON BATCH UNIT

Taken (g)		Reaction conditions		Obtained							Theoretical yield (%)	Selectivity (%)
Phenol	VCH	Temp. (°C)	Rate of vol. Flow (h ⁻¹)	Phenol (unused)	VCH (unused)	Target product	Intermediate product	Residue	Total	Losses		
94	108	60	0.5	57.2	61.3	77.8	3.0	1.2	200.5	1.5	37.5	96.1
94	108	80	0.5	47.4	49.9	98.4	2.8	1.3	199.8	2.2	48.7	95.8
94	108	90	0.5	34.5	37.4	123.8	1.6	2.2	199.5	2.5	61.3	96.6
94	108	110	0.5	22.5	27.5	146.3	1.3	1.7	199.3	2.7	72.4	97.7
94	108	120	0.5	29.4	33.6	121.4	8.3	6.6	199.3	3.7	60.1	89.4
94	54	110	0.5	68.8	30.6	37.9	4.6	4.3	146.2	1.8	37.5	81.2
94	108	110	0.5	22.5	27.5	146.3	1.3	1.7	199.3	2.7	72.4	97.7
94	162	110	0.5	32.4	60.8	140.8	12.6	6.6	253.2	2.8	69.7	87.6
94	216	110	0.5	37.7	131.4	115.5	8.4	13.6	306.6	3.4	57.2	84.2
94	108	110	0.2	20.9	26.9	133.9	13.6	4.7	200.0	2.0	66.3	87.9
94	108	110	0.5	22.5	27.5	146.3	1.3	1.7	199.3	2.7	72.4	97.7
94	108	110	0.7	29.9	37.7	128.5	1.3	1.4	198.8	3.2	63.6	95.0
94	108	110	1.0	41.5	47.8	104.4	3.0	2.5	199.2	2.8	51.7	94.8

TABLE-2
PHYSICO-CHEMICAL PROPERTIES OF *p*-(CYCLOHEXENYLETHYL)PHENOL

Structural formula	T _{boil.} °C/5 mm Hg	n _D ²⁰	ρ ₄ ⁴⁰	m.w.		Elemental analysis (%):			
				Calcd.	Found	Calcd.		Found	
						C	H	C	H
	147-148	1.5445	1.0040	202	202	83.2	8.9	83.9	9.4

2920 and 2845 cm⁻¹ and also the bands at 1345, 1108 cm⁻¹, characterizing δ_{CH₂} in the cycle. Methyl group is characterized by deformational vibrations at 1460 and 1370 cm⁻¹.

As seen from Table-2, the molecular weight, elemental composition of the synthesized compound corresponds to the calculated values. Analyzing the experimental data, it is concluded that phosphorus-containing zeolite-Y, in comparison with

other catalysts, is more efficient catalyst for cycloalkenylation of phenol with 4-vinylcyclohexene.

Tri-[*p*-cyclohexenylethyl]phenyl]phosphite (CAPH) was synthesized and tested as an antioxidant in turbine oil T-46 by interacting *p*-(cyclohexenylethyl)phenol with phosphorus trichloride. The experiments were carried out in a four-necked flask equipped with a thermometer, a separatory funnel, a stirrer

TABLE-3
 PHYSICO-CHEMICAL PROPERTIES OF TRI-[*p*-(CYCLOHEXENYL)PHENYL]PHOSPHITE

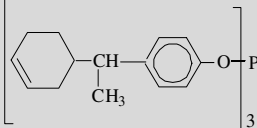
Structural formula	Empirical formula	T _{boil.} °C/5 mm Hg	n _D ²⁰	ρ ₄ ⁴⁰	m.w.
	C ₄₂ H ₅₁ O ₃ P	321-324	1.5715	1.0782	634

 TABLE-4
 COMPARATIVE TEST RESULTS OF TRI-[*p*-(CYCLOHEXENYL)PHENYL]PHOSPHITE

Nominations	Sediment (%)	Viscosity (mm ² /sec, 100 °C)		Δν (%)
		Pre-test	Post-test	
Turbine oil T-46 (without addition of antioxidant)	2.17	7.90	8.75	10.76
T-46 + IKhP-21	0.90	8.63	9.25	7.18
T-46 + CAPH	0.15	8.56	8.37	3.80

and a glass tube for supplying of nitrogen to the system. *p*-(Cyclohexenylethyl)phenol and toluene were added to the flask in a calculated amount and heated. At 40 °C, phosphorus trichloride was added dropwise using additional funnel. After the addition of phosphorus trichloride, the reaction temperature was raised to 50-80 °C and the mixture was stirred for 2 to 5 h again. The hydrogen chloride is removed from the reaction through esterification in the presence of nitrogen gas atmosphere. Separated hydrogen chloride is trapped in an aqueous solution of NaOH.

After the completion of esterification reaction, the reaction mixture was transferred to Claisen flask and rectified, at first, phosphorus trichloride and a solvent were distilled at atmospheric pressure and then, unreacted *p*-(cyclohexenylethyl)phenol and the target product tri-[*p*-(cyclohexenylethyl)phenyl]phosphite were distilled in the vacuum (at 10 mm Hg). For the purpose of determining the optimal reaction conditions that ensure the maximum yield of tri-[*p*-(cyclohexenylethyl)phenyl]phosphite, the temperature varied from 40 to 80 °C with constant stirring from 1 to 5 h and the molar ratio of tri-[*p*-(cyclohexenylethyl)phenyl]phenol to phosphorus trichloride (1:1::4:1).

Analysis of the results obtained in the synthesis of tri-[*p*-(cyclohexenylethyl)phenyl]phosphite makes possible to determine the optimum conditions for the phosphatization of *p*-(cyclohexenylethyl)phenol with phosphorus trichloride, which are: temperature 70 °C, reaction time 4 h, the molar ratio of *p*-(cyclohexenylethyl)phenol to PCl₃, 3:1. Under these conditions, the theoretical yield of the target product is 88.6 %. The physico-chemical parameters of tri-[*p*-(cyclohexenylethyl)phenyl]phosphite are given in Table-3.

In IR spectra, the typical adsorption bands of tri-[*p*-(cyclohexenylethyl)phenyl]phosphate were identified as the bands at 1505 cm⁻¹ is due to skeleton vibrations of benzene ring and the bands at 825 cm⁻¹ refers to non-planar deformational C-H vibrations of *p*-substituted aromatic nuclear. Adsorption bands at 2920-2845 cm⁻¹ refers to valence vibrations of cyclohexene ring and CH₃ groups. Deformational vibrations of C-H bond of CH₃-group are confirmed by the adsorption band in the field of 1370 cm⁻¹. Intensive adsorption bands in the field of 1230 and 1190 cm⁻¹ refer to valence vibrations of P-O-C bonds.

PMR spectrum of tri-[*p*-(cyclohexenylethyl)phenyl]phosphite consists of three signals of resonance adsorption: singlet in the

field of δ = 1.3 ppm, corresponding to methyl proton, multiplying signal in the field of δ = 1.35-1.70 ppm, corresponding to the protons of cyclohexene ring and quadruplet A₂B₂ spin system in the field of δ = 6.95 ppm, referring to the protons of aromatic nuclear, but singlet in the field of 5-6 ppm, shifted by dilution to strong field of (1H)-OH-group.

Synthesized tri-[*p*-(cyclohexenylethyl)phenyl]phosphite was tested as an antioxidant of turbine oil T-46. The experiments were carried out on DK-NAMI apparatus in comparison to GOST 11063-77 at 100 °C in 30 h, in the amount of the antioxidant of 0.5 % mass. The results of comparative tests are shown in Table-4.

As seen from Table-4, addition of phosphite to the base oil leads to improvement of its antioxidative properties. The best efficiency is observed in the presence of phosphite, its application allows accretion of oil viscosity (Δν) at 100 °C amounts to 3.8 %, but sediment amount, formed after oxidation of 30 h-0.15 %; in the absence of base oil of antioxidant, correspond to 10.76 and 2.17 %. Hence, the compound tri-[*p*-(cyclohexenylethyl)phenyl]phosphite can be recommended as antioxidant for the turbine oil T-46.

Conclusion

Cycloalkenylation of phenol with 4-vinylcyclohexene was carried out in the presence of zeolite-Y catalyst, saturated by orthophosphoric acid on the batch unit. As a result, it was found out that at optimum regime the yield of the target product *p*-(cyclohexenylethyl)phenol amounts to 72.4 % of theory on the phenol taken, but selectivity to 97.7 % on the target product.

Phosphatization of *p*-(cyclohexenylethyl)phenol with phosphorus trichloride allows obtaining of tri-[*p*-(cyclohexenylethyl)phenyl]phosphite with the yield of 88.6 % and its investigation as an antioxidant for turbine oil T-46 resulted effectively.

REFERENCES

1. B.N. Gorbunov, Y.A. Gurchich and I.P. Maslova, Chemistry and Technology of Stabilizers of Polymeric Materials, Khimiya, Moscow, p. 315 (1981).
2. Ch.K. Rasulov, A.G. Azizov, V. G. Mirzoev, R.K. Azimova, S.I. Abasov and S.Z. Alieva, *Petroleum Chem.*, **49**, 377 (2009); <https://doi.org/10.1134/S0965544109050065>.
3. V.G. Mirzayev, *Process. Petrochem. Oil Refining*, **17**, 93 (2015).

4. A.M. Magerramov, M.R. Bairamov, G.M. Mekhtieva, M.A. Agaeva, P.Sh. Mamedova, D.M. Kulieva and I.G. Mamedov, *Russ. J. Appl. Chem.*, **80**, 665 (2007); <https://doi.org/10.1134/S1070427207040295>.
5. E.V. Kabilyanskiy and I.M. Vasilkevich, *Issue Chem. Chemical Technol.*, **44**, 102 (2008).
6. D.K. Korenev, V.A. Zavorotniy, V.B. Kelarev and T.A. Lagutina, *Chem. Technol. Fuels Oils*, **39**, 72 (2003); <https://doi.org/10.1023/A:1023297405336>.
7. Ch.K. Rasulov, A. H. Azizov, R.K. Azimova, E.M. Abdullaev and S.I. Abasov, *Petroleum Chem.*, **52**, 352 (2012); <https://doi.org/10.1134/S0965544112050106>.
8. A.F. Markov, A.E. Prosenk and Y.Sh. Shvarch, *Chem. Pharm. J.*, **45**, 117 (2005).
9. K.I. Dyubchenko, V.V. Nikulina and E.I. Terax, *Petroleum Chem.*, **45**, 1 (2005).
10. I.V. Aleksandrova, Z.R. Tushakova and I. Lomakin, *Oil Refining Petrochem.*, **12**, 29 (2012).
11. J. Kang, X. Wang, X. Peng, Y. Yang and K. Cheng, Q. Zhang and Y. Wang, *Ind. Eng. Chem. Res.*, **55**, 13008 (2016); <https://doi.org/10.1021/acs.iecr.6b03810>.
12. N. Boonprakob, W. Chomkitichai, J. Ketwaraporn, A. Wanaek, B. Inceesungvorn and S. Phanichphant, *Eng. J. (N.Y.)*, **21**, 81 (2017); <https://doi.org/10.4186/ej.2017.21.1.81>.