

SOME FEATURES OF CYCLOALKYLATION REACTION OF P-CHLOROPHENOL WITH 1-METHYLCYCLOALKENES

S.T. Shahmuradov

Acad. Y. Mammadaliyev Institute of Petrochemical Processes
National Academy of Sciences of Azerbaijan
30, Khojali ave., AZ 1025, Baku, Azerbaijan
e-mail: shahmuradov_samir@mail.ru

Received 01.11.2019

Abstract: 2(1-methylcyclopentyl)- and 2(1-methylcyclohexyl)-4-chlorophenols were synthesized by the interaction of *p*-chlorophenol with 1-methylcyclopentene and 1-methylcyclohexene in the presence of zeolite-Y catalyst impregnated on ortho-phosphoric acid in a continuously operating installation. It revealed that the yield of the desirable products - 2(1-methylcycloalkyl)-4-chlorophenols was 72.5-74.7% according to the calculation amount of *p*-chlorophenol at 110-120°C reaction temperature, molar ratio of *p*-chlorophenol to cyclene of 1:1 and 0.5 h⁻¹ vol. rate. The selectivity was 93.0-96.3% according to the target product.

Keywords: *p*-chlorophenol, 1-methylcyclopentene, 1-methylcyclohexene, zeolite Y containing phosphorus, cycloalkylation, 2 (1-methylcycloalkyl)-4-chlorophenol

Introduction

Due to their low toxicity, alkyl phenols are used primarily in medical supplies, in the production of food packaging etc. Spatially hindered phenols are widely used as food additives, which have a number of advantages from the point of view of food technology: high antioxidant effects with relative high thermal stability, low toxicity, and low cost [1-6].

Successful practices of the use of antioxidants in the polymer, rubber, food, and cosmetic industries testify to good prospects of the use of these compounds in materials which contacted with humans. Chemical additives containing halide fragments are important among these compounds. They raise fire resistance of polyolefins' service life by preventing destruction from external factors' impact (temperature, light, etc.) [7-12].

Chlorophenol antioxidants are studied until now and described in the literature they are extremely diverse in their structure Well-known alkylchlorophenols are mainly obtained by alkylation of chlorophenols with aliphatic hydrocarbons; however, they are not fully combined with polyolefin and unstable at high temperatures. In this regard cycloalkyl chlorophenols dissolve well and they are combined with polyolefin and they are thermo stable.

The article presents the results of research into the interaction of *p*-chlorophenol (PChPh) with 1-methylcyclopentene (1-MCP) and 1-methylcyclohexene (1-MCH) in the presence of a Zeolite-Y catalyst impregnated with orthophosphoric acid on a continuously operating installation.

Experimental section

To obtain 2(1-methylcycloalkyl)-4-chlorophenols freshly distilled *p*-chlorophenol, 1-methylcyclopentene with bp = 74-75 °C, $n_D^{20} = 1.4347$, $\rho_4^{40} = 0.7782$, with 98% purity and 1-methylcyclohexene with bp = 110-111 °C, $n_D^{20} = 1.4500$, $\rho_4^{40} = 0.8200$, 99.8% purity were used.

The orthophosphoric acid was impregnated with Zeolite-Y and used as a catalyst. The catalyst was prepared by means of vigorous mixing of the alumo gel with the zeolite Y type of catalyst of cracking (SiO₂/Al₂O₃ 4.8, the degree of exchange of Na⁺ ions for H⁺ ions 97%). The obtained product was molded through filter (1.6 mm diameter), then granulated and calcined.

Then the catalyst was impregnated with 10% solution of phosphoric acid (according to the calculated amount of P_2O_5), evaporated and dried in the oven at 100 °C temperature and calcined with a continuously rising temperature from 200 °C to 600 °C.

Cycloalkylation of para-chlorophenol with 1-methylcycloalkenes was carried out in a laboratory setup.

p-Chlorophenol and cyclene were supplied to the mixer from the tank in the desired ratio. The temperature of p-chlorophenol was maintained at 40°C. After PChPh mixing with cyclene, the mixer was fed into the reactor bottom. A mixture of components passed through a layer of catalyst, cooled in a refrigerator and collected in a container.

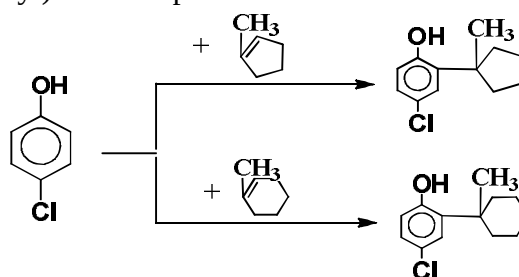
If rectified at atmospheric pressure, cyclene and PChPh (up to 200°C) were distilled off, and then the desired reaction product was isolated under vacuum (10 mm Hg), its purity and physico-chemical parameters determined. The composition and the structure of the obtained products were determined via the chromatography and spectral analysis methods.

Chromatographic analysis of the alkylation product was analyzed on LCM-72 chromatograph with a thermal conductivity detector. Column length is 2 m, solid carrier - chromanized N-AW-DMC, washed acid and salinized with dimethyldichlorosilane, fr. 0.2-0.25 mm. The stationary phase is 5% methyl siloxane elastomer SE-30. Intake and final temperatures of the column were 50°C and 270°C respectively. Programmed speed is 10°C/min, helium carrier gas speed is 50 ml/min., temperature of the source is 365°C, detector temperature is 300°C and the speed of the chart tape is 60 mm/h. For calculation, internal normalization method was used on the basis of conversion to 100% of total peak areas.

The structure of the synthesized product was determined via IR- and 1H NMR spectroscopy. IR spectrum of the samples was recorded on ALPHA Furey spectrometer (company BRUKER, Germany) in the interval of 600-4000 cm^{-1} . 1H NMR spectrum was recorded on «Bruker-300» (Germany) at a room temperature and CCl_4 with internal standart - tetramethylsiloxane.

Results and discussion

Interaction of p-chlorophenol with 1-methylcyclopentene and 1-methylcyclohexene in the presence of Zeolite-Y catalyst impregnated with orthophosphoric acid proceeds with the formation of 2(1-methylcycloalkyl)-4-chlorophenols:



In order to identify the optimal conditions for ensuring of the maximum yield of 2(1-methylcycloalkyl)-4-chlorophenols, an effect of temperature, molar ratio of PChPh to 1-methylcycloalkene and vol. rate on the yield and composition of reaction products were studied.

The reaction temperature varied from 80 to 140 °C, the molar ratio of PChPh to 1-methylcycloalkene ranged from 0.5: 1 to 1: 0.5 mol/mol, and the vol. rate was from 0.2 to 0.8 h^{-1} .

Figure 1 shows the results of experiments on the cycloalkylation of p-chlorophenol with 1-methylcyclopentene in the presence of a catalyst.

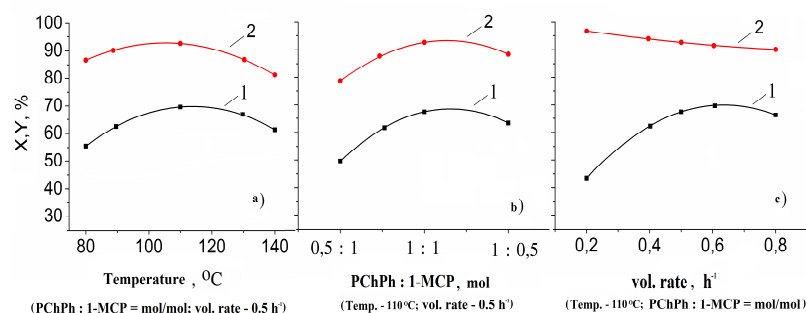
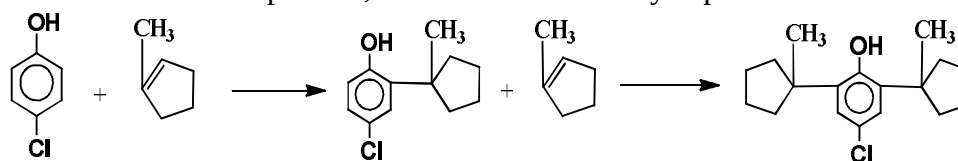


Fig. 1. Dependence of the yield X (%) (1) and the selectivity of Y (%) (2) 2(1-methylcyclopentyl)-4-chlorophenol from the temperature (a), molar ratio of the initial components (b) and the vol. rate (c).

At 110°C temperature the highest yield of the desirable product of 2(1-methylcyclopentyl) -4-chlorophenol is achieved - 72.5%; increasing the temperature prior to 140°C leads to a decrease the yield and selectivity of the product to 61.8% and 84.2%, respectively. The yield of 2(1-methylcyclopentyl)-4-chlorophenol was 72.5% at the the molar ratio of p-chlorophenol to 1-MCP is equaled to 1: 1 and the further increasing the amount of p-chlorophenol or cyclene does not give positive results, and the yield of the whole product remains at the same level. The prolonged staying of 2-monosubstituted p-chlorophenol in the reaction zone creates the conditions for joining the second cyclene molecule that resulting in the production of the disubstituted product, which is confirmed by experimental dates.



When increased the volume rate of the reaction from 0.2 to 0.5 h⁻¹ cause an increase the yield of 2(1-methylcyclopentyl)-4-chlorophenol from 44.5 to 72.5%. Also a further increasing the flow rate does not lead to an increase the yield of the target product.

Thus, optimal conditions for obtaining 2 (1-methylcyclopentyl) -4-chlorophenol were revealed: a reaction temperature was 110°C, molar ratio of p-chlorophenol: 1-MCP = 1: 1, vol. rate was 0.5 h⁻¹. Under these conditions, the yield of the desired product was 72.5% (according to the calculation), and the selectivity of the target product was 93.0%.

The similar results were obtained for 2 (1-methylcyclohexanol) -4-chlorophenol.

Analysis of the obtained results made it possible to establish the optimal conditions for the interaction of PCP with 1-MCH in the presence of zeolite containing phosphorus: temperature 120° C, molar ratio of PCP:1-MCH of 1:1 mol/mol, vol. rate - 0.5 h⁻¹. In this condition the yield of 2 (methyl-cyclohexyl) -4-chlorophenol was 74.7% according to the calculation of taken PCP, and selectivity was 96.3% for the desired product.

The IR spectrum results for 2 (1-methylcyclohexyl) -4-chlorophenol are given in Table 1.

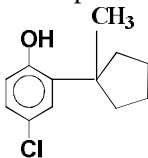
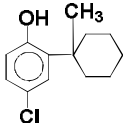
Table 1. Results of IR analysis of the 2(1- methyl cyclohexyl)-4-chlorophenol

Absorption band	Location in the structure
654, 705 sm ⁻¹	C – Cl bond
809, 879 sm ⁻¹	1, 2, 4 substituted benzene ring
973 sm ⁻¹	C – H bonds of cyclohexane ring
1114, 1171 sm ⁻¹	C – O bond

1245 cm^{-1} , 3555 cm^{-1}	deformation and valence vibration corresponding to the O – H bond on the OH group
1322, 1400, 1450, 1489 cm^{-1}	deformation vibration of C – H bond for CH_3 and CH_2 groups
2856, 2923 cm^{-1}	valence vibration of CH_3 and CH_2 groups
1597 cm^{-1}	C – H bonds of benzene ring
1698 cm^{-1}	C – H bonds of benzene ring

Below-cited are ^1H NMR analysis results of 2 (1-methylcycloalkyl) -4-chlorophenols.

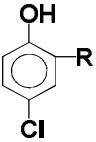
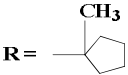
Table 2. Results of the ^1H NMR spectroscopic analysis of 2(1-methylcycloalkyl)-4-chlorophenols

№	Chemical name and structure	type of proton	chemical shift, ppm.
1.	2(1-methyl cyclopentyl)-4-chlorophenol 	CH_3 – singlet	0.95
		CH_2 (cycle) – wide signal	1.4-1.5
		OH – singlet	6.0
		H_1, H_2 and H_3 protons of the benzene ring as multiplete	6.8-7.0
2.	2(1-methylcyclohexyl)-4-chlorophenol 	CH_3 – singlet	0.873
		CH_2 (cycle) – wide signal	1.3-1.4
		OH – singlet	6.0
		H_1, H_2 и H_3 (benzene ring) multiplete	6.8-7.2

In the spectrum of ^{13}C NMR of 2 (1-methylcyclohexyl) -4-chlorophenol, the carbon atom of the CH_3 group at $\delta = 62$ ppm (singlet), carbon atoms of the aromatic ring $\delta = 117.85$; 123.7; 126; 127.65; 129; 137.5; 154.8 ppm (singlet), carbon atoms of cyclohexene $\delta = 24.87$; 26.4; 29.0; 36.3; 38.0 ppm (singlet) were observed.

Table 3 presents physical and chemical indicators of 2(1-methylcycloalkyl)-4-chlorophenol.

Table 3. Physical and chemical indicators of 2(1-methylcycloalkyl)-4-chlorophenol

	boiling point at 10 Hg.	n_D^{20}	ρ_4^{40}	molar mass	element composition, %			
					calculated		found	
					C	H	C	H
 $\text{R} =$	198-202	1.5025	1.0095	210	68.6	7.1	68.3	6.9
	207-211	1.5176	1.0308	224	69.6	7.6	69.4	7.3

According to Table 3, the revealed element composition of synthesized compounds complied with the calculated amount of elements.

Conclusion

The interaction reaction of *p*-chlorophenol with 1-methylcyclopentenyl and 1-methylcyclohexene was studied in the presence of Zeolite-Y impregnated orthophosphoric acid impregnated with ortho-phosphoric acid on a continuously operating installation. It was determined that at 110-120 reaction temperature, molar ratio of *p*-chlorophenol to cyclene of 1:1 mol/mol and at vol. rate 0.5 h⁻¹ the yield of the desirable product– 2(1-methylcycloalkyl)-4-chlorophenol was 72.5-74.7 % according to the taken PCP and the selectivity was – 93.0-96.3 % for target product.

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P-XLORFENOLUN 1-METİLTİKLOALKENLƏRLƏ TSİKLOALKİLLƏŞMƏ REAKSİYALARININ BƏZİ XÜSUSİYYƏTLƏRİ

S.T. Şahmuradov

AMEA Neft-kimya prosesləri institutu
AZ 1025, Bakı, Xocalı pr., 30
e-mail: shahmuradov_samir@mail.ru

p-Xlorfenolun orto-fosfat turşusu hopdurulmuş seolit Y katalizatoru iştirakında fasiləsiz işləyən qurğuda 1-metiltsiklopenten və 1-metiltsikloheksenlə qarşılıqlı təsirindən 2(1-metiltsiklopentil)- və 2(1-metiltsikloheksil)-4-xlorfenolların sintezi həyata keçirilmişdir. Müəyyən edilmişdir ki, 110-120°C temperaturda, *p*-xlorfenolun tsiklenə 1 : 1 mol nisbətində, 0.5 saat⁻¹ həcmi sürətində məqsədli məhsulların - 2(1-metiltsikloalkil)-4-xlorfenolun çıxımı götürülən *p*-xlorfenola görə 72.5-74.7%, seçicilik məqsədli məhsula görə 93.0-96.3% təşkil edir.

Açar sözlər: *p*-xlorfenol, 1-metiltsiklopenten, 1-metiltsikloheksen, fosfor tərkibli seolit Y, tsikloalkilləşmə, 2(1-metiltsikloalkil)-4-xlorfenol

НЕКОТОРЫЕ ОСОБЕННОСТИ РЕАКЦИИ ЦИКЛОАЛКИЛИРОВАНИЯ П-ХЛОРФЕНОЛА С 1 – МЕТИЛЦИКЛОАЛКЕНАМИ

С.Т. Шахмурадов

Институт нефтехимических процессов Национальной АН Азербайджана
AZ 1025, Баку, пр.Ходжалы 30
e-mail: shahmuradov_samir@mail.ru

Осуществлен синтез 2(1-метилциклопентил)- и 2(1-метилциклогексил)-4-хлорфенолов, взаимодействием *p*-хлорфенола с 1-метилциклопентеном и 1-метилциклогексеном в присутствии катализатора цеолита Y, пропитанного орто-фосфорной кислотой, на непрерывно действующей установке. Установлено, что при температуре 110-120°C, мольном соотношении *p*-хлорфенола к циклену 1:1 моль/моль и объемной скорости 0,5 час⁻¹ выход целевых продуктов - 2(1-метилциклоалкил)-4-хлорфенолов составил 72.5-74.7 % от теории на взятый *p*-хлорфенол, а селективность 93.0-96.3 % по целевому продукту.

Ключевые слова: *p*-хлорфенол, 1-метилциклопентен, 1-метилциклогексен, фосфорсодержащий цеолит-Y, циклоалкилирование, 2(1-метилциклоалкил)-4-хлорфенол