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ABSTRACT

SYNTHESIS OF CYCLOALKYLCHLOROPHENOLS' AMINOMETHYL DERIVATIVES AND STUDY OF THEIR APPLICATION FIELDS

Specialty: 2314.01 – Petrochemistry

Field of science: Chemistry

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INTRODUCTION

Actuality of the subject and the approbation. Leading countries in the world are now focusing on improving the quality of polymeric materials, rubbers, oils and fuels rather than their quantity. For this reason, the production of chemical additives has become widespread, and alkylphenol compounds are most important ones among them. So, that 70-75% of industrially used chemical additives is obtained on the basis of alkylphenols. Recently, new application fields of alkylphenols have been being identified. They are widely used as ligands for catalytic precursors used in olefins oligomerization and polymerization processes, as pesticides, insecticides, bactericidal and disinfectant medicinal preparations in various areas of agriculture.[1] But alkylphenol-based chemical additives don't meet constantly growing demand of industry. The known alkylphenol-based chemical additives aren't completely soluble in the materials in which they are used, they aren't thermally stable, environmentally friendly and efficient from technological point of view and etc.

In this regard, the dissertation work is devoted to an actual problem – synthesis of monocycloalkyl-4-chlorophenols and polyfunctional, combined chemical additives by their interaction with amines as a result of alkylation reactions of parachlorophenol with methylcyclenes in the presence of КУ-23 and ortho-phosphate acid-impregnated Zeolite-Y catalysts, determination of their qualitative properties and recommendation for industrial use.

The object and the subject of the research. The object of the research is studying of the effect of parachlorophenol in the presence of cationite and zeolite-containing catalysts with cyclic hydrocarbons of different structures and various kinetic parameters on the direction of cycloalkylation reactions; the subject of the research is testing Mannich bases of obtained cycloalkyl-chlorophenols in scientifically substantiated fields.

The aim and objectives of the work. The main goal of the work is synthesizing 2-mono-methylcycloalkyl-4-chlorophenols

[1] Ч.К.Расулов Синтез N-[2-гидрокси-4(5)-метил- и 5-(метилциклогексил)бензил]-морфолинов-антиоксидантов для трансформаторных масел/ //Журнал прикладной химии, -2010. т.83, № 12, - с. 2013-2016.

otained as a result of catalytic cycloalkylation reactions of para-chlorophenol with various-structured cyclenes and aminomethyl-cycloalkylchlorophenols containing chloro, hydroxyl, nitrogen fragments by involving them to amonimethylation reactions with isopropylamine, morpholine, piperidine and testing them as thermal stabilizers in polypropylene, ligands for catalytic precursors used in ethylene oligomerization process, insecticides against Colorado betles in potatoes, green worms and fungi in vegetables, acaricides against ticks in small- and large-horned animals.

The following tasks have been fulfilled to achieve the goal:

- 2-methylcycloalkyl-4-chlorophenols have been synthesized in the result of cycloalkylation reactions of para-chlorphenol with 1-methylcyclopentene, 1(3)-methylcyclohexenes, isoprene cyclodimers in the presence of КУ-23 and ortho-phosphate acid-impregnated Zeolite-Y catalysts;
- aminomethylation reactions of obtained 2-methylcycloalkyl-4-chlorophenols with formaldehyde, isoproopylamine, morpholine and piperidine have been studied and physical-chemical properties and chemical structures of the synthesized compounds have been determined;
- the synthesized substances have been tested as thermal stabilizers for polypropylene, ligands for catalytic precursors used in ethylene oligomerization, insecticides against Colorado beetles in potatoes, green worms and herbs in vegetables, as well as bactericides and disinfectants against gut microbes in cattles.

Research methods. Catalytic cycloalkylation reactions of para-chlorphenol with cycloolefins, obtaining Mannich bases in the result of obtained 2-cycloalkyl-4-chlorophenols aminomethylation reactions have been performed on the batch devices in laboratory.

Basic provisions for defense. Cycloalkylation reactions of para-chlorophenol with methylcycloalkenes in a new catalytic system; obtaining Mannix bases as a result of aminomethylation reactions of synthesized methylcycloalkylchlorophenols with isopropylamine, morpholin and piperidine; testing of cycloalkylchlorophenols as thermal stabilizers in polypropylene, use of their aminomethyl de-

rivatives as ligands for catalytic precursors in ethylene oligomerization process, as insecticides against agricultural pesticides and diseases, desinfectants and acaricides.

Scientific novelty of the research. For the first time, cycloalkylation reactions of para-chlorophenol with 1-methylcyclopentene, 1- and 3-methylcyclohexenes, isoprene cyclodimers have been systematically studied in the presence of КУ-23 and ortho-phosphate acid-impregnated Zeolite-Y catalysts.

The effect of the cyclenes structures and mode parameters taken for cycloalkylation reactions has been studied on the yield, selectivity of the target products and the reaction direction.

For the purpose of widening the scope of scientific research carried out on Mannich bases and identify new fields of their use, for the first time, 22 new substances - 2-aminomethyl-4-chloro-6-methylcycloalkylphenols have been synthesized by studying the interactions of 2-cycloalkyl-4-chlorophenols with formaldehyde, amines (isopropylamine, morpholine, piperidine), their physical-chemical properties have been studied and application fields have been identified. 2 Azerbaijani and 1 Eurasian patents have been got on the researches carried out.

Theoretical and practical significance of the research. A theoretical idea have been formed in advance on their efficient properties as a result of complex analysis of the synthesized chemical compounds containing hydroxyl, chlorine and nitrogen fragments, scientific justification of the researches carried out. 2-Methylcycloalkyl-4-chlorophenols have been tested as thermal stabilizers in polypropylene, 2-morfolino and 2-piperidinomethyl-4-chloro-6-cycloakylphenols – as ligands for catalytic precursors used in ethylene oligomerization process. Besides, isopropylaminomethylphenol has been tested as an insecticide against Colorado beetles in potatoes, green worms and herbs in vegetables, as well as bactericides and disinfectants against gut microbiota in cattles.

The author's personal presence. All of the results reflected in the dissertation have been achieved by the author himself. The issues, experiments and tests, systematization, interpretation and gen-

eralization of the results have been made by the author's direct participation.

The accuracy of the results. Cycloalkylchlorophenols and their aminomethylation products obtained by the interaction of p-chlorophenol with cycloolefins have been studied using modern methods - IR, ^{1}H and ^{13}C spectra, elemental analysis, electrical conductivity, X-ray diffractograms available in the latest model devices.

Publications. 28 scientific papers have been published on the dissertation work including 11 papers, 2 Azerbaijani and 1 Eurasian patents, 14 International and republician conference theses.

Approbation. The results of the dissertation work has been reported and discussed at the following conferences: the VII All-Russian zeolite conference “Zeolites and small porous materials: achievements and prospects” (Zvenigorod, 2015); International scientific-practical conference "Actual problems of modern biology and chemistry" devoted to national leader Haydar Aliyev’s 92nd and 94th anniversaries (Ganja, GSU 2015, 2017); the III International scientific-practical conference of young researchers (Baku, 2015), republician scientific conference “Lubricants, fuels, special fluids, additives and reagents”, dedicated to the 50th anniversary of the academician A.Guliyev Institute of Chemistry of Additives (Baku, 2015), republician scientific conference devoted to T.Shahtakhtinski’s 90th anniversary (Baku, 2015), the IX republician scientific conference "Actual problems of chemistry" (Baku, BSU, 2015), the IV republician scientific conference “Actual problems of ecology and soil science in the 21st century” (Baku, BSU, 2015), the III republician scientific conference “Modern problems of chemistry of monomers and polymers” (Sumgayit, SSU, 2015), the IV International scientific conference of young researchers (Baku, 2016), the IX Baku International Mammadaliyev Conference on Petrochemistry (Baku, 2016), republician scientific conference on “Macromolecules chemistry, organic synthesis and composite materials” (Sumgait, 2016),International scientific conference on “Functional monomers and polimer materials of special peculiarities” (Sumgait, SSU, 2017), Republician scientific-technical conference on “Fuels, fuel components, special liquids, oils and

additives" devoted to prof. S.A.Sultanov's 90th anniversary (Baku, 2017), International scientific-technical conference on "Petrochemical synthesis and catalysis in complex condensed systems" devoted to academician B.G.Zeynalov's 100th anniversary (Baku, 2017), International conference "Naghiyev readings" devoted to academician M.Naghiyev's 110th anniversary (Baku, 2018), International scientific conference on "Technology and technique of petrochemistry and oil-gas production" (Omsk, 2018).

The name of the organization where the dissertation work was performed. The dissertation work was performed at the laboratory of "Synthesis and technology of alkylphenols" on the scientific-research work plan of Y.H. Mammadaliyev Institute of Petrochemical Processes of ANAS (State registration number 0114Az2005. 2017-2019).

The scope and structure of the work. The dissertation consists of 179 pages, including introduction, 5 chapters, results, 192 references and appendices. There are 24 tables and 37 figures in the dissertation.

Introduction deals on the actuality, aim, scientific novelty and practical significance of the work.

The first chapter is a literature review and analysis of the literature resources on obtaining methods for alkylcycloalkylphenols in the result of phenol, chlorophenols alkylation reactions with olefins and cycloolefins and simultaneously obtaining Mannich bases of alkylphenols. The chapter also provides critical analysis of existing research in this area and the scientific directions of the research have been justified.

The second chapter is the experimental part. It is about the initial raw materials, their physical-chemical properties, the course of the experiments, description of the deviced used, analysis methods for the target products obtained by cycloalkylation and aminomethylation reactions.

The third chapter has been devoted to the study of alkylation reactions of para-chlorophenol with 1- and 3-methylcyclohexenes, isoprene cyclodimers in the presence of КУ-23 catalyst.

The fourth chapter deals on the study of para-chlorphenol alkylation reactions with 1(3)-methylcycloalkens, isoprene cyclodimers in the presence of ortho-phosphate-impregnated Zeolite-Y catalyst, the influence of various parameters on the yield and selectivity of the obtained products.

The fifth chapter is about studying of 2-methylcycloalkyl-4-chlorophenols aminomethylation reactions with isopropylamine, morpholine and piperidine, obtaining Mannich bases and determining of their physical-chemical properties. This chapter also deals on the use of the synthesized 2-morfolinomethyl and 2-piperidinomethyl-4-chloro-6-methylcycloalkylphenols as thermal stabilizers in polypropylene, as ligands for catalytic precursors in ethylene oligomerizastion process, the tests carried out on the use of isopropylaminomethylphenol in agriculture against Colorado beetles in potatoes, insecticides against green worms and herbs in vegetables, as well as bactericides and disinfectants against ticks in cattles.

The dissertation work ends in the results as a summary of the scientific research, list of the literature resources referred and appendices.

THE MAIN CONTENT OF THE WORK

Initial raw materials, catalysts, rules for carrying out the tests and analysis methods for the reaction products

Para-chlorophenol, 1-methylcyclopenten, 1- and 3-methylcyclohexenes, 1-methyl-3-isopropenylcyclohexene-1-il(diprene), 1-methyl-4-isopropenylcyclohexene-1-il(dipentene), a mixture of isoprene cyclodimers (160-180^{o}C fraction) have been taken as raw materials and benzene, hexane, toluene, isooctane – as solvents for the researches. КУ-23 (GOST 20298-74) and phosphate-impregnated Zeolite-Y catalysts have been used as catalysts for alkylation reactions.

Phosphorous-containing Zeolite-Y catalyst is developed on the following method: alumogel cracking catalyst (Zeolite-Y, SiO_2:Al_2O_3=4.8, ion exchange rate 97%) is perfectly mixed. The obtained mass is scrapped through a sieve of 1.6 mm diameter, grinded and become incandescent. Further, the 10% ortho-phosphate acid (according to P_2O_5) is impregnated into the catalyst and evaporated,

dried in oven at 100°C, and becomes incandescent by increasing of temperature from 200 to 600 °C. Further, the catalyst is cooled down and used.

Para-chlorophenol (PCP) alkylation reactions by cycloolefins have been carried out in three-necked flask under laboratory conditions, catalyst is extracted by filtration after the reaction and rectified. Methylcycloolefins distillation is followed by the distillation of para-chlorophenol and the reaction products under vacuum.

Mannich-based reactions of the synthesized 2-cycloalkyl-4-chlorophenols with formaldehyde and amines have been carried out in a three-necked flask.

Chromatographic analysis of the reaction and rectification products have been realized on LXM-72 chromatograph.

The molecular mass has been identified on MX-1303 mass-spectrometry at 200°C.

Densities of the products synthesized have been determined by pneumatic method, refraction coefficients by refractometry on "IRF-22" device (Russia).

IR spectra of the obtained cycloalkylchlorophenols and their Mannich bases have been drawn on "ALPHA IR Furye" (AFR) spectrometers produced by "BRUKER" and "Spectrum BX" companies of "Perkin-Elmer" company. The NMR spectra of the obtained compounds have been drawn on 300 mHz NMR spectrometer (AFR) produced by "BRUKER".

The elemental composition of the obtained substances has been determined on "Leco Europe B.V." (VOUERSWEG 118-6161 AG GELEEN-NEDERLAND; Postbuus 1174-6160 BO GELLEN) device. The electrical conductivities of the synthesized products are determined by the Hungarian CONDUCTIVE TVPE: ok-102/1 conductometer.

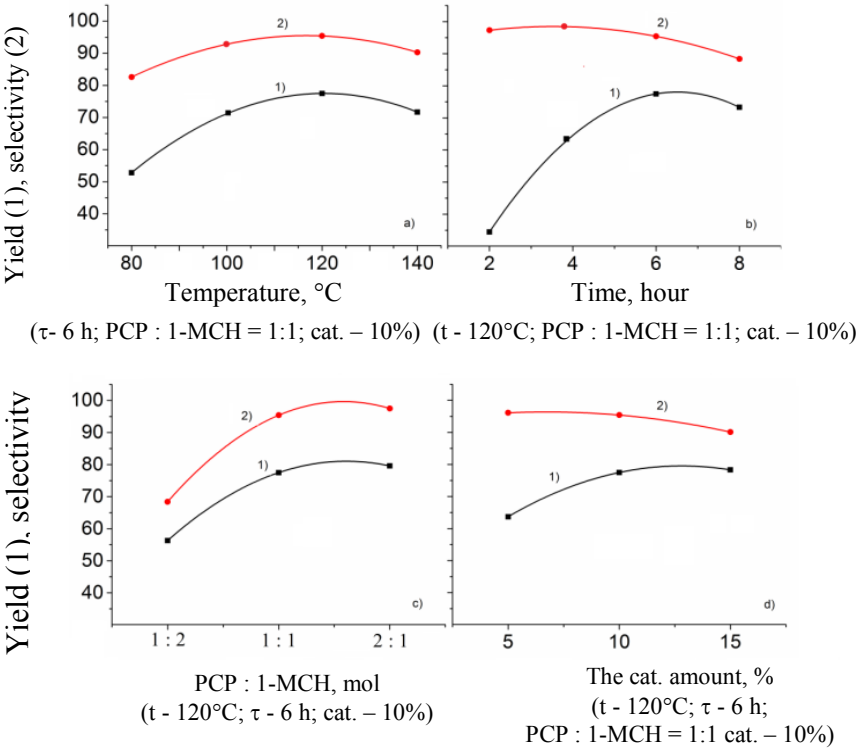
Differential scanning calorimeter (DSC) has been used to study polymers with stabilizer additives. This method has allowed to measure glass, melting (up to 1000°C), crystallization points, starting temperature of oxidation, heat capacity and other quantities. X-ray diffractograms of the samples synthesized have been drawn on

PANanalytical EMPYREAN X-ray Phase Analyzer. The samples have been analyzed on the device using λCuKα irradiation.

Interactions of para-chlorophenol with methylcyclenes in the presence of КУ-23 catalyst

Catalytic cycloalkylation reactions of para-chlorophenol with 1-methylcyclopentene, 1(3)-methylcyclohexenes, diprene and dipentene have been studied at 80-140°C for 2-8 h, at 1:0.5÷2 molar ratios of PCP to cyclene in 5-15% amount of catalyst (on the taken PCP).

The results of catalytic alkylation reactions of para-chlorophenol with 1-methylcyclohexene in the presence of catalyst КУ-23 are illustrated below:



(τ- 6 h; PCP : 1-MCH = 1:1; cat. – 10%) (t - 120°C; PCP : 1-MCH = 1:1; cat. – 10%)

Fig. 1. Dependent curves of 2-(1-methylcyclohexyl)-4-chlorophenol yield (1) and selectivity (2) on temperature (a), time (b), mol ratios of initial components (c), catalyst (d)

As is evident from Fig. 1, efficient yield (77.5%) and selectivity (95.4%) of the target products can be achieved at 120°C by cycloalkylation reaction.

The yields of the target products are 34.5 and 60.1%, respectively, selectivity - 97.3-96.0% by 2- and 4-hours contact of the initial components with the catalyst. In 6-hour reaction time, the target product yield and selectivity are 77.5 and 95.4%, which may be considered acceptable. Increasing the reaction time to 8 hours doesn't have a positive impact on the yield and selectivity of the product, they amount to 73.3% and 88.4%, respectively.

As seen from the results of the tests, it's expedient to take the initial components in the ratio of 1:1 to have efficient yield and selectivity of the target product.

The target product yield is 63.7% in 5% amount of catalyst for the reaction; by increasing of the catalyst amount for 2 times, that's to say taking of 10% of a catalyst, the yield (77.5%) and selectivity (95.4%) of the target products may be considered satisfactory.

So, optimal conditions have been found for PCP catalytic cycloalkylation reaction with 1-methylcyclohexene in the presence of КУ-23 catalyst. There have been determined, that the yield of the target product according to the taken PCP is 77.5%, selectivity – 95.4% by cycloalkylation reaction carried out at 120°C for 6 hours in 10% of the catalyst amount and 1:1 mol ratios of the initial components.

Alkylation reactions of PCP with other cycloolefins in the presence of КУ-23 catalyst have been carried out by the same way.

Interaction reactions of para-chlorophenol with methylcyclenes in the presence of ortho-phosphate-impregnated Zeolite-Y catalyst

Interaction reactions of para-chlorophenol with 1-methylcyclopentene, 1(3)-methylcyclohexenes, diprene, dipentene and isoprene cyclodimer fraction of 160-180°C have been studied in the presence of ortho-phosphate acid impregnated Zeolite-Y catalyst. For example, let's take a look on cycloalkylation reaction of para-chlorophenol with 1-methylcyclohexene.

The following conditions have been found for PCP cycloalkyltion reaction with MCH : reaction temperature - 80-140°C, duration – 2-8 h, mol ratio of PCP to 1-MCH - 0.5÷2:1, the catalyst amount – 5-15% (on PCP). Cycloalkylation reactions results are illustrated in Fig.2.

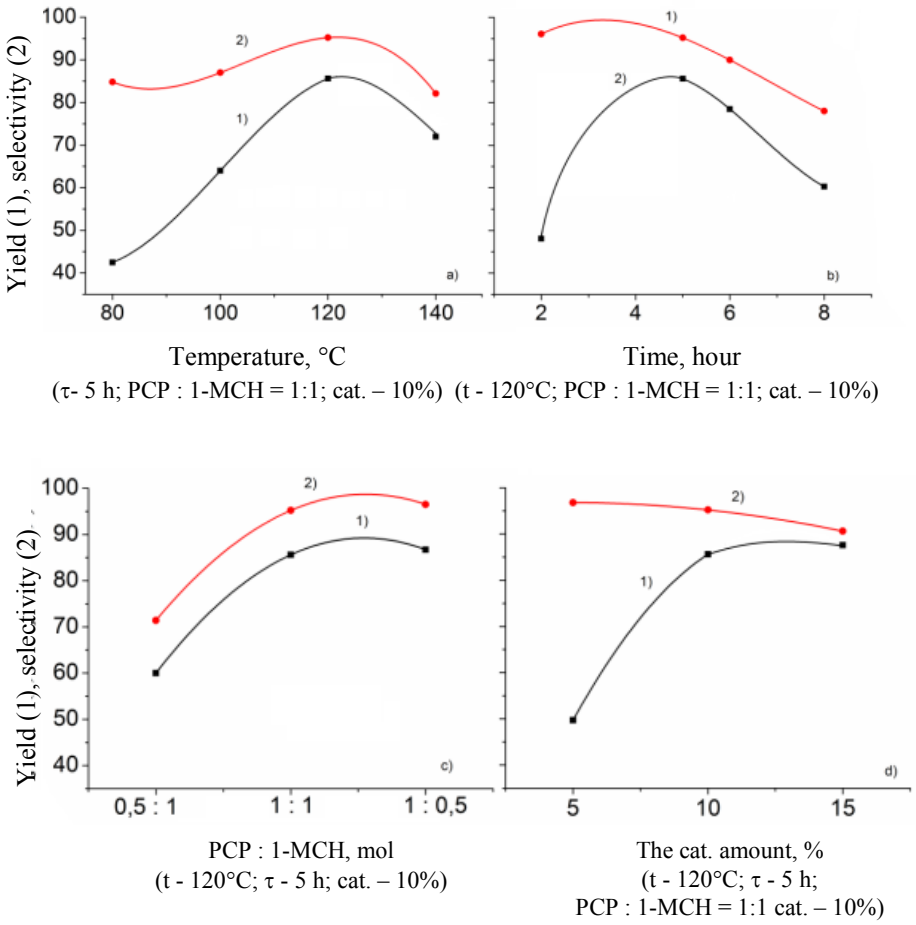


Fig.2. Dependent curves of 2(1-methylcyclohexyl)-4-chlorophenol yield (1) and selectivity (2) on temperature (a), time (b), mol ratios of initial components (c) and catalyst amount (d)

Increase in the reaction temperature from 80 to 110 ^{o}C causes increase in the target product yield from 42.5 to 85.6%, and selectivity from 84.8 to 95.2%.

As is seen from the Figure, the target product yield and selectivity can be considered satisfactory in 5-hour contact time of the components with the catalyst. So, that the yield is 85.6, but selectivity 95.2%. Increasing the reaction time is not effective in this case.

1:1 mol ratio of PCP to MCH allows to have high yield and selectivity. The yield and selectivity are much lower by increasing 1-MCH concentration in the reaction mixture: 60.1 and 71.4%, correspondingly. Low indices of the yield and selectivity prove the increase in 2,6-di-substituted PCP amount in the reaction products.

The catalyst amount has a significant role for studying PCP cycloalkylation reaction with 1-MCH. 5% of catalyst amount isn't sufficient for cycloalkylation reaction. In this case, the yield amounts to 49.7%, but selectivity 96.8%. The target product yield increases from 85.6 to 87.6%, but selectivity amounts to 95.2-90.6% by the increase of the catalyst amount about 7-15%. But large amount of the catalyst isn't considered efficient from industrial point of view. Therefore, 7% of the catalyst amount has been accepted for the reaction.

Therefore, efficient conditions have been found for PCP cycloalkylation reaction with 1-MCH in the presence of ortho-phosphate impregnated Zeolite-Y catalyst: reaction temperature - 110^{o}C, time - 5 h, mol ratio of PCP to 1-MCH – 1:1, the catalyst amount on PCP – 7%. The yield of the target product – 2(1-methylcyclohexyl)-4-chlorophenol on PCP amounts to 85.6%, but selectivity on the target product is 95.2%.

As a result of the investigations, there have been proved, that cycloalkylation products of PCP in the presence of newly used КУ-23 and phosphate acid impregnated Zeolite-Y catalysts, presented by us are obtained with high yields and selectivities than the known catalysts. Table 1 shows cycloalkylation reactions results of PCP with 1-MCH in the presence of different catalysts.

Table 1

The results of the known and presented catalytic cycloalkylation reactions of para-chlorophenol with 1-methylcyclohexene

Catalysts	$NaHSO_4$ (known)	KY-2 (known)	KY-23	Zeolite-Y H_3PO_4
Temperature, ^oC	120	120	120	110
Time, h	4.5	6	6	5
PCP : 1-MCH, mol	2 : 1	1 : 1	1 : 1	1 : 1
The catalyst amount, %	10	10	10	7
Content of cycloalkylation products,% mas.				
Methylcycloalkylchlorophenyl ether	1.8	2.3	1.4	–
2-Monocyclohexkyl PCP	93.1	90.5	92.6	96.7
2,6-di-cyclohexyl PCP	3.4	5.2	4.8	2.8
Residue	1.7	2.0	1.2	0.5
Yield, %	69.8	72.3	77.5	85.6
Selectivity, %	91.2	89.7	94.4	95.2

As seen from Table 1, the catalysts presented by us, especially ortho-phosphate impregnated Zeolite-Y catalyst allow to carry out cycloalkylation reactions under the soft conditions: cycloalkylchlorophenyl ether isn't obtained in the end product, the yield and selectivity are high (85.6-95.2%).

Alkylation reactions of PCP with other cycloolefins have also been studied by the same way.

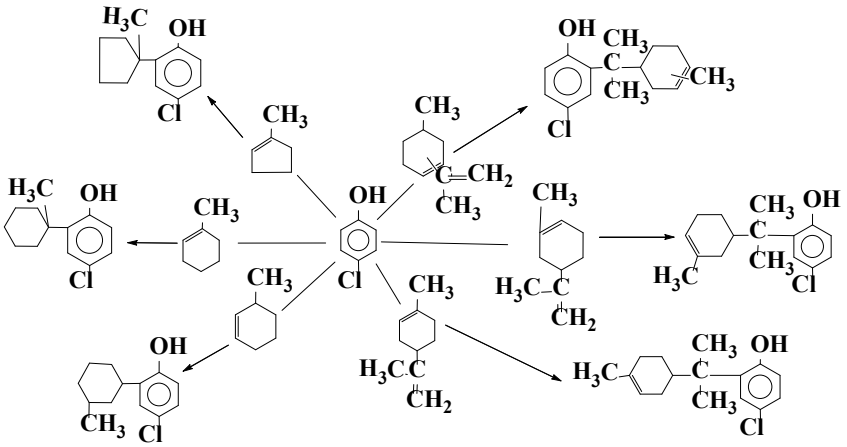


Fig. 3. The scheme of para-chlorophenol catalytic alkylation reactions with methylcyclenes

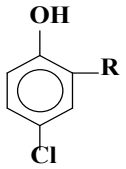
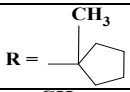
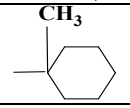
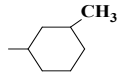
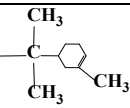
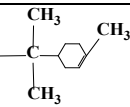
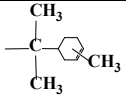
The effect of temperature, time, mol ratios of initial components and the catalyst amount have been studied on the yield and selectivity of 2-cycloalkyl-4-chlorophenols which are the products of para-chlorophenol alkylation reactions with 1-methylcyclopentene, diprene, dipentene and isoprene cyclodimer mixture (160-180 ^{o}C fraction). There have been determined, that the yield of the target products – 2-methylcycloalkyl-4-chlorophenols amounts to 61.2-77.5% (on PCP), selectivity is 87.3-95.4% at 110-140°C reaction temperature, time of 4-6 hours, 1:1 mol ratios of PCP to cycloolefins and 10-15% of catalyst amount (on the taken PCP).

So, in the result of alkylation reactions of para-chlorophenol with 1-methylcyclopentene, 1- and 3-methylcyclohexenes, isoprene cyclodimers in the presence of ortho-phophate impregnated Zeolite-Y catalyst, the yield of the target product has been determined as 65.8-85.6% (on the taken PCP), and selectivity on the target product - 89.4-95.2% at 110-130 ^{o}C of reaction temperature, 4-6 hours of reaction time, 1:1 mol ratio of PCP to cyclenes, 7-10% of catalyst amount.

Physical-chemical properties of the synthesized 2-methylcycloalkyl-4-chlorophenols have been determined and the results have been set into Tab.2.

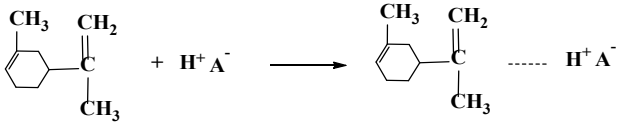
Table 2

Physical-chemical properties of 2-methylcycloalkyl-4-chlorophenols

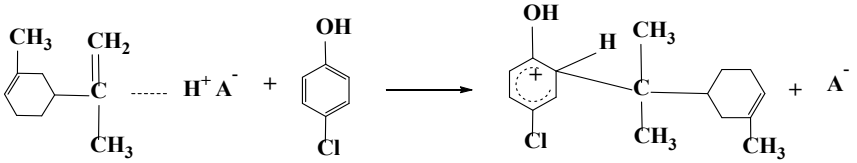
	Boiling point, 10 mm Hg	n_D^{20}	ρ_4^{40}	Mol mas.	Elemental composition, %			
					Calc.		Found	
					C	H	C	H
	198-202	1.5025	1.0095	210	68.6	7.1	68.3	6.9
	207-211	1.5176	1.0308	224	69.6	7.6	69.4	7.3
	204-208	1.5108	1.0137	224	69.6	7.6	69.1	7.2
	217-220	1.5153	1.0228	265	72.6	7.9	72.0	7.4
	221-225	1.5208	1.0279	265	72.6	7.9	72.3	7.7
	219-223	1.5173	1.0254	265	72.6	7.9	72.2	7.5

Let's look through a possible mechanism of catalytic cycloalkylation reactions of para-chlorophenol with isoprene cyclodimers in the example of the PCP alkylation with DP.

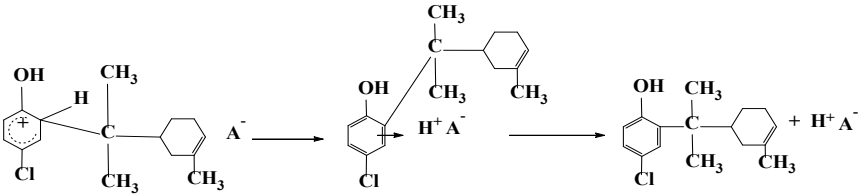
At first, a "catalyst-cyclene" polarization complex is formed by interaction of the catalyst and DP.



The polarization complex is converted into carbocation, which in turn interacts with the benzene ring of PCP to form the π-complex:



covalent bonds are formed between isopropylcyclohexenyl substituent and carbon atom of aromatic ring by reconversion of π-complex into δ-complex; at this time, the electron interaction of the hydroxyl group is condensed by the Cl atom, and the favorable conditions for the formation of the δ-complex with the carbon atom in the ortho-state are created. δ-complex is unstable and easily converts to π-complex. The latter stabilizes by giving its proton and forming of 2- (isopropyl-3-methylcyclohexene-3-il) -4-chlorophenol:



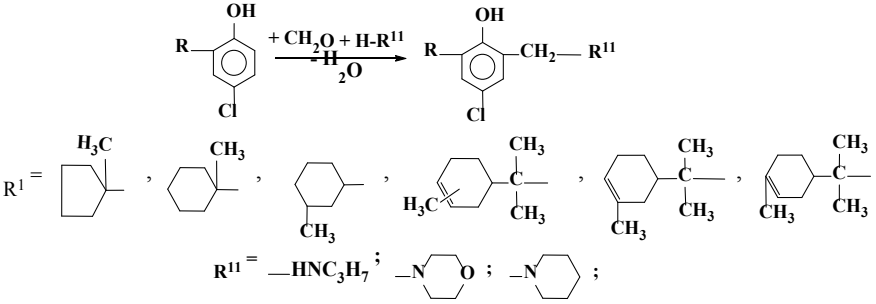
It's important to note one point. There are two different natured double bonds in diprene: one in the side chain and the other in the cycle. Cyclohexene double bond is more stable than double bond in the isopropenyl fragment in the side chain. For this reason, at first, the catalyst produces carbocation by interaction with the isopropenyl fragment of diprene. More severe conditions are required for the reaction of diprene with cyclohexenyl fragment.

Aminomethylation reactions of 2-methylcycloalkyl-4-chlorophenols with isopropylamine, morpholine and piperidine

Phenol, para-chlorophenol, 2-cycloalkyl-4-chlorophenols, isopropylamine, morpholine, piperidine (after redistillation) and 30% of formaline have been used for the studies.

Aminomethylphenols have been obtained by the interaction of phenol or para-chlorophenol and formaldehyde, amine at 1:1:1 mol ratios. Calculated amount of phenol (or para-chlorophenol), amine

and benzene are poured and stirred in a three-necked flask. 30% of formaldehyde is added into the reaction mixture at 25-30°C by drops and the mixture is stirred for another hour. Later, the reaction mixture temperature is raised to 75-80°C and the process is continued for a further 2 hours. The reaction products are washed by water to release non-reacted formaldehyde and amine, later treated by chloride acid and NH_4OH. Amine is released from water and benzene by rectification, then residual product is rectified under low pressure and the structures, compositions and physical-chemical properties of the products are determined.

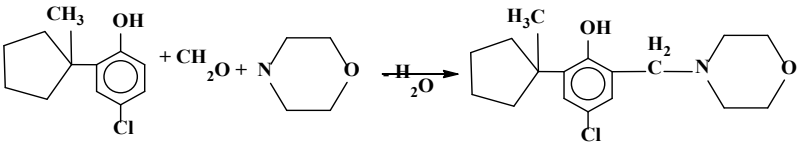


For example, the aminomethylation reactions of 2-methylcycloalkyl-4-chlorophenols with formaldehyde and morpholine are looked through below: calculated amount of 2-methylcycloalkyl-4-chlorophenol, morpholine and benzene are poured into a flask and stirred by heating to 30-40°C. At this temperature, 30% of formaldehyde solution is added into the mixture. The reaction temperature is raised up to 80°C and stirred for 2 hours.

The reaction products are purified from other initial and by-products by washing and rectified under low pressure.

Synthesis of 2-morpholinomethyl-4-chloro-6(1-methylcyclopentyle)-phenol

Aminomethylation reactions run on the following equation:



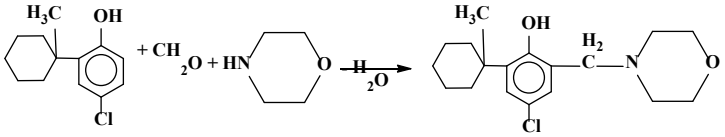
21.0 g of 2(1-methylcyclopentyle)-4-chlorophenol, 50 ml of benzene and 7.6 g morpholine are added into three-necked flask and heated. 10 g of 30% formaldehyde solution is dropped onto the mixture through dropping funnel at 30°C. After dropping of solution, the reaction mixture is heated at 70°C within 2 hours. The experiment is continued on the above-mentioned method. The target product is rectified under low temperature; meantime 27.9 g of 2-morpholinomethyl-4-chloro-6(1-methylcyclopentyl)-phenol is obtained and it amounts to 75.7% of theoretical yield.

The following absorption bands are observed in IR spectrum of 2-morpholinomethyl-4-chloro-6(1-methylcyclopentyl)-phenol: naphthene ring is observed in 585, 887, 1070, 1110 and 1350 cm^{-1}, C=C bonds of benzene rings - in 1500 cm^{-1} absorption bands; deformational and valence shifts of C-H bond in CH_2 and CH_3 groups – in 3000-2800 cm^{-1}, hydroxyl group – in 3510-3120 cm^{-1}, ortho-substituents of benzene ring – in 756 cm^{-1}, C-Cl bond – in 640 cm^{-1}, -NH group – in 1256 cm^{-1} absorption bands.

The protones of the following functional groups have been observed in ^1H NMR spectrum of the synthesized 2-morpholinomethyl-4-chloro-6(1-methylcyclopentyl)-phenol: CH_3 – singlet in 0.97 m.h.; CH_2-spread signal in cycle – in 1.7-1.8 m.h.; OH-group proton – in 6.5 m.h. as a singlet; H_1, H_2, H_3 protons as multiple – in 6.7-7.3. m.h.

Synthesis of 2-morpholinomethyl-4-chloro-6-(1-methlcyclohexyl)-phenol

The synthesis has been carried out on the following reaction:



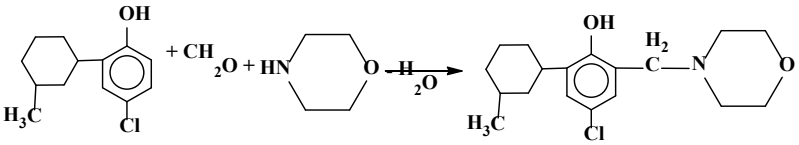
7.6 g of morpholine, 50 ml of benzene are added to 22.5 g of 2(1-methylcyclohexyl)-4-chlorophenol and heated and followed by dropping of 10.0 g of 30% formaldehyde at 30°C. The experiment is continued by above-mentioned methodics. The target product is released by rectification under low pressure, chemical structure and physical-chemical properties are determined. In the result, 30.0 g of

2-morpholinomethyl-4-chloro-6-(1-methylcyclohexyl)-phenol is obtained and it reveals that the yield of the target product amounts to 78.4%.

The results of the substance IR and ^{1}H NMR spectra are corresponding to the previous Mannich base spectra.

Synthesis of 2-morpholinomethyl-4-chloro-6(3-methylcyclohexyl)-phenol

Aminomethylation reactions run on the following equation:

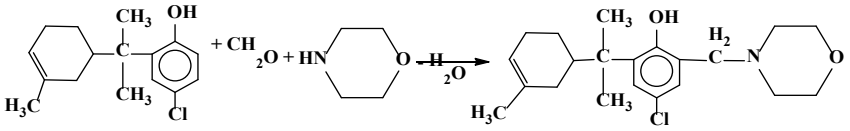


The initial components amount taken for the reaction and the conditions for the experiment are corresponding to the results of the previous experiment. In the result, 28.3 g of 2-morpholinomethyl-4-chloro-6(3-methylcyclohexyl)-phenol is obtained and it reveals that the yield of the target product amounts to 73.8%.

IR and ^{1}H NMR spectra of 2-morpholinomethyl-4-chloro-6-(3-methylcyclohexyl)-phenol are corresponding to the previous substance spectra.

Aminomethylation reactions of the cycloalkylchlorophenols obtained on the basis of isoprene cyclodimers with formaldehyde and morpholine

Interaction reaction of 2(3-methylcyclohexenylisopropyl)-4-chlorophenol obtained by alkylation of para-chlorophenol with diprene, with formaldehyde solution and morpholine runs on the following equation:

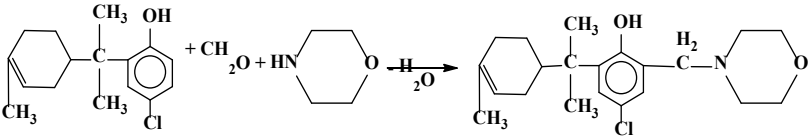


7.6 g of morpholine, 50 ml of benzene and 10.0 g of formaldehyde are added into a flask and heated. 26.5 g of 2(3-methylcyclohexenylisopropyl)-4-chlorophenol is added on it part by part at 40°C of the reaction temperature. Then, the reaction

temperature is increased to 80°C and stirring is continued for 2.5 h at this temperature. Later, the mixture is purified by washing on the above-mentioned method and undergone rectification. In the result, 32.2 g of the target product is obtained and it reveals, that the yield amounts to 76.1% according to the taken cycloalkylchlorophenol.

Chemical structures and physical-chemical properties of the synthesized 2-morpholinomethyl-4-chloro-6(3-methylcyclohexenyl-isopropyl)-phenol have been determined.

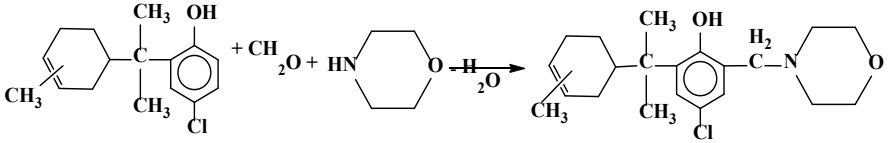
Aminomethylation reaction of 2-(4-methylcyclohexenyl-isopropyl)-4-chlorophenol obtained on the basis of dipentene with formaldehyde and morpholine has been carried out on the same method:



The amount of the initial raw materials taken for aminomethylation reaction, the experiment conditions are corresponding to the properties of the above-mentioned experiment.

30.1 g of 2-morpholinomethyl-4-chloro-6(4-methylcyclohexenyl-isopropyl)-phenol is obtained by the rectification of the reaction products and the yield amounts to 72.3%.

Aminomethylation reactions of isoprene cyclodimers-based 2[3(4)-methylcyclohexenylisopropyl]-4-chlorophenol with formaldehyde and morpholine have been realized on the above-mentioned methodics.



It's resulted in obtaining 31.5 g of 2-morpholinomethyl-4-chloro-6[3(4)-methylcyclohexenylisopropyl]phenol that the yield is 76.5% according to the initial raw material.

Application fields of the synthesized Mannich bases

2(Cycloalkyl)-4-chlorophenols have been tested as thermal stabilizers in polypropylene. The a-PP used for verification is an intermediate product of Polypropylene Plant of Tomsk Petrochemical PU, with an average molecular weight of 38000, polydispersity of 5, 3, number of the bonds per 1 mol equals to 0.4.

The diffractograms of a-PP and its samples prepared after the addition of a stabilizer have been studied on PANalytical EMPYREN X-ray diffractometer of Netherland production, and thermooxidation stability by Jupiter 449F3 of NETZSCH analyzer.

There have been carried out thermal analyses of the used a-PP and the polymer prepared by the addition of 2(1-methylcyclohexyl)-4-chlorophenol to it in the amount of 0.5% mas. As a result of the tests it has been established that the stabilizer-added polypropylene, suggested by us, remains stable until 445°C thermooxidation in contrast to the known thermal stabilizers.

New catalysts have been synthesized by the interaction of the aminomethylation products of the synthesized 2-cycloalkyl-4-chlorophenols with $ZrCl_4$ in cooperation with laboratory 30 of academician Y.H.Mammadaliyev Institute of Petrochemical Processes of ANAS and have been used in ethylene oligomerization process.

The complex compounds synthesized by interaction of 2-morpholinomethyl- and 2-piperidinomethyl-4-chlorophenols as ligands in different mol ratios with $ZrCl_4$, have been tested as a component of heterogenized metal complex catalytic system in ethylene oligomerization and polymerization processes. There have been determined, that heterogenized zirconium complexes synthesized on the basis of 2-morpholinomethyl and 2-piperidinomethyl-4-chlorophenols and the oligomer product obtained by ethylene oligomerization in the presence of $(C_2H_5)_2AlCl$ as co-catalyst mainly consist of C_4-C_{10} fraction of linear α-olefins and this fraction amounts to 80-90% in the oligomer product depending on ligand content and reaction conditions. It also consists of *the synthesized ligands* in the presence of zirconium complex synthesized on the basis of 2-piperidinomethyl-4-chlorophenol and

(C_2H_5)$AlCl_2$ as co-catalyst, in aliphatic solvents (heptane, hexane and etc.) and *polyethylene oil fraction* in Al:Zr=(25-30):1 mol ratio of the catalytic system components under 1.8-5.0 MPa pressure, modified ethylene oligomerization product at 90°C of the reaction temperature with 57.5-67.5% yield.

It has been determined, that the yield of the target products is higher (80-85%) than the known catalysts (70-75%) by the use of chlorobenzylamines as ligands for the catalysts in the oligomerization of C_4-C_{10} olefins.

4-Isopropylaminomethlphenol (IAPh) has been tested as an insecticide against Colorado beetles in potatoes in the region farms by Jalilabad Support point of Azerbaijan Research Institute of Viticulture and Wine-making.

Initial tests of the insecticides have been mainly carried out under field conditions. The insecticide tests against Colorado beetles in potatoes have been carried out using different target rates per hectare: 200, 300 and 500 g. IAF-1 insecticide at a rate of 200 g per hectare showed a technical efficiency of 83.2%, at a rate of 300 g - 88.4% and 95% at a rate of 500 g. No fight has been made against the pesticide in the control variant.

The IAPh-1 medicinal preparation has been tested as an insecticide against greenworms in vegetables. The medicinal preparation has technical efficiency of 98%. The tests have been compared with "Fostak" imported from Germany and it has been determined that they had the same technical effectiveness.

Aminomethylation products of 2-cycloalkyl-4-chlorophenols and 4-isopropylamineophenol have been presented to the Scientific-Research Institute of Veterinary under the Ministry of Agriculture of Azerbaijan to study the bactericidal and disinfectant effects of intestinal microbes on poultry, large and small horned animals. In the result of the tests, only isopropylaminophenol has more efficient results than about 30 medicinal preparations presented from different institutes.

As a result of the experiments carried out on the study of bactericidal effects of the preparations on the test objects against intestinal microbes, it has been found out that only 0.5% water solution of iso-

propylaminophenol completely neutralizes E. coli for 15 min.

The disinfectant property of isopropylaminophenol against intestinal bacteria has been studied on wooden test objects. It has been found that 10% solution of this substance has been completely disinfected from the E. coli microbe at 18-20°C, with a solution of 1*l* per 1 m^2 area in 2-hours exposition.

The test results reveals that isopropylaminophenol disinfection effect on intestinal microbes is shown in 1 day: it completely disinfects intestinal germs.

CONCLUSIONS

1. For the first time, alkylation reactions of para-chlorophenol with 1- and 3-methylcyclohexenes, isoprene cyclodimers have been studied in the presence of КУ-23 catalyst. There have been determined, that the yield of the target products – 2-methylcycloalkyl-4-chlorophenols amounts to 61.2-77.5%, selectivity on the target product is 87.3-95.4% at 110-140 ^{o}C of the reaction temperature, within 4-6 h, at 1:1 mol ratios of PCP to cycloolefins, 10-15% of the catalyst (on the taken PCP) [7-11,14,17,19,21].
2. Catalytic alkylation reaction of para-chlorophenol with 1-methylcyclopentene, 1- and 3-methylcyclohexenes, isoprene cyclodimers has been carried out in the presence of orthophosphate acid impregnated Zeolite-Y catalyst. 65.8-85.6% of yield (on the taken PCP) and 89.4-95.2% of selectivity of the target products have been determined at 110-130°C reaction temperature, within 4-6 h, at 1:1 mol ratio of PCP to cyclenes and 7-10% of catalyst amount [3,4,8,12,15,16,19,25].
3. The Mannich bases of 2-mono-(cycloalkyl)-4-chlorophenols have been obtained by the realization of their aminomethylation reactions with isopropylamine, morpholine and piperidine. Simultaneously, for the first time 4- and 2-mono-aminophenols have been obtained by phenol, para-chlorophenol aminomethylation reactions carried out with isopropylamine, morpholine and piperidine. It has been resulted in synthesizing of 22 new structured chemical substances [1,2,6,13, 27,28].

4. 2-Mono-(cycloalkyl)-4-chlorophenols have been tested as thermal stabilizers in polypropylene. As a result of the studies it has been determined, that 2-mono-(cycloalkyl)-4-chlorophenols-added polypropylene remains stable to 445°C thermooxidation in differ from the known thermal stabilizers [5,18,20,24].
5. 2-mono-(cycloalkyl)-4-chloro-6-aminophenols have been used as ligands for the catalytic precursors used in ethylene oligomerization process. There have been determined, that the yield of the target products are higher (80-85%) than the known catalysts (70-75%) by the use of chlorobenzylamines as ligands for the catalysts used in C_4-C_{10} olefins oligomerization process [13,24].
6. Synthesized 4-isopropylaminophenol has been tested as an insecticide against the Colorado potato beetle, which is widespread in agriculture, against green worms in vegetables. The tests have been compared with the medicinal preparation "Fostak" of Germany. 4-Isopropylaminophenol showed the same efficiency (95-96%) as "Fostak" [22].
7. 4-Isopropylaminophenol has been tested as bactericidal and disinfectant medicinal preparations against intestinal germs in other fields of agriculture - in poultry, small- and large-horned animals. There have been determined, that 0.5% water solution of 4-isopro-pilaminophenol inactivates intestinal germs within 15 min. Aqueous solution of 10% of the preparation per 1 m^2 area, at 18-20°C temperature of the solution completely neutralizes the E. coli microbe at wood-test facilities [23,26].
8. Technical-economic properties of 4-isopropylaminophenol medicinal preparation have been calculated. There have been determined, that the cost of one ton of 4-isopropylaminophenol is 2300 AZN. The cost of medicinal preparation bought from "Fostak" (Germany) for the same purpose is $ 5.000 / ton.

THE FOLLOWING SCIENTIFIC PAPERS HAVE BEEN PUBLISHED ON THE DISSERTATION MATERIALS:

1. Abbasov, V.M., Rasulov, Ch.G., Shahmuradov, S.T., Panahov, T.M., Asadullayev, R.A. Study of the synthesis and properties of 2-aminomethyl-4-cycloalkylphenols complex salts" // Proceedings of International scientific-practical conference on "Actual problems of modern biology and chemistry", – Ganja: –GSU, – May 5-6, –2015, –p. 90-93.
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