Republic of Azerbaijan

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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

SYNTHESIS OF AMINOMETHYL DERIVATIVES OF STERICALLY HINDERED METHYLCYCLOALKYLPHENOLS AND THEIR APPLICATION IN THE ANALYSIS OF CERTAIN HEAVY METALS

Speciality: 2306.01- "Organic chemistry"

Field of Science: Chemistry

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GENERAL CHARACTERİSTİCS OF THE WORK

Relevance of the topic and degree of investigation. Alkylphenols constitute one of the most extensively studied and widely applied fields of chemistry, while still requiring further comprehensive investigation[1]. Their broad range of performance properties, availability of raw materials, and the simplicity of production technologies account for their widespread utilization. Alkylphenols are mainly employed as antioxidants, stabilizers, additives, plasticizers, and related functional compounds in polymeric materials, rubbers, lubricating oils, and fuels. At present, more than 75% of the chemical additives used in industry are produced on the basis of alkylphenols.

In recent years, new application areas of alkylphenols and their nitrogen-containing derivatives have continued to emerge. These compounds have been successfully utilized as ligands in the preparation of transition-metal complexes applied in the oligomerization of olefins, as well as analytical reagents for the determination of certain heavy metals in industrial and natural samples[2].

From this point of view, the present dissertation research is devoted to a highly relevant field involving the synthesis of Mannich reaction bases via the aminomethylation of alkylation products obtained from the reactions of phenols with cycloolefins possessing various cyclic structures, using formaldehyde and piperidine, as well as the investigation of their potential application areas.

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[1]Расулов, Ч.К., Агамалиев, З.З., Гасанова, Г.Д., Нагиева, М.В. Синтез алкилфенолов и применение их в реакциях аминометилирования.− Баку: Муаллим, – 2021, – 197 с.

[2]Rasulov, Ch.K. Aminomethylation reactions of 2-[1(3)-methylcycloalkhyl]-4methylphenols with piperidine / Chingiz Rasulov, Ali Zalov, Gulnar Huseynova, Husu Ibrahimov, Reyhan Aliyeva, Matlab Khamiyev // Processes of Petrochemistry and Oil Refining, − Baku: − 2024. Vol. 25. No 3, − pp. 712-720.

Object and subject of the research. The object of the conducted research comprises the aminomethylation reactions of cycloalkylphenols possessing various cyclic structures with piperidine. The subject of the study involves the determination of the effective application fields of the synthesized piperidinomethyl-cycloalkylphenols.

Purpose and objectives of the research. The main purpose of the research is the synthesis of Mannich reaction bases, namely 2-piperidinomethylcycloalkylphenols, via the aminomethylation reactions of sterically hindered cycloalkylphenols with piperidine, followed by the investigation of their practical application areas. In particular, the synthesized compounds were examined as ligands for catalytic precursors employed in the oligomerization of ethylene, as antioxidants for diesel fuel, and as analytical reagents for the determination of heavy metals in various objects.

To achieve the stated objective, the following research tasks were carried out:

- the aminomethylation reactions of para-methylcycloalkyl-phenols obtained by the alkylation of phenol with five- and six-membered cyclic hydrocarbons in the presence of piperidine were investigated, and the material balances for the synthesis processes of the target products were calculated;

- the aminomethylation reactions of 2-methylcycloalkyl-4-methylphenols, synthesized via the alkylation of *p*-cresol with 1-methylcyclopentene, 1(3)-methylcyclohexenes, diprene, dipentene, and the 160–180°C fraction of isoprene cyclodimers, with piperidine were investigated, and the material balances for the preparation processes of the Mannich bases were determined;

- the chemical structures and physicochemical properties of the newly synthesized compounds were established;

- the synthesized piperidinomethylcycloalkylphenols were tested as ligands in catalytic precursors employed for the oligomerization of ethylene, as antioxidants for diesel fuel, and as analytical reagents for the determination of heavy metals in industrial and natural objects.

Research Methods. The aminomethylation reactions of sterically hindered methylcycloalkylphenols with formalin and piperidine were carried out under laboratory conditions using a batch-type reactor setup.

Reliability of the results. The chemical structures and properties of the starting materials, namely sterically hindered methylcycloalkylphenols, as well as the synthesized Mannich reaction bases derived from them, were investigated using modern analytical methods, including IR, ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and chromatographic techniques.

Main provisions submitted for defense. The aminomethylation reactions of sterically hindered methylcycloalkylphenols obtained by the alkylation of phenol and *p*-cresol with cyclic hydrocarbons of various structures in the presence of piperidine were carried out. The synthesized piperidinomethylcycloalkylphenols were applied as ligands for catalytic precursors used in the oligomerization of ethylene, as antioxidants for diesel fuel, and as analytical reagents for the determination of certain heavy metals in various objects.

Scientific novelty of the research. For the first time, the aminomethylation reactions of para-methylcycloalkylphenols, 2-methylcycloalkyl-4-methylphenols, phenol, and *meta*- and *para*-cresols with formalin and piperidine were investigated. The influence of the chemical structures of the synthesized compounds on their properties was studied. As a result of the conducted research, 15 compounds possessing novel chemical structures were synthesized. Azerbaijani patents were obtained for the newly synthesized compounds.

Theoretical and practical significance of the research. Piperidinomethylcycloalkylphenols synthesized via the interaction reactions of sterically hindered methylcycloalkylphenols with piperidine were evaluated as ligands in catalytic precursors used for the oligomerization of ethylene, as antioxidants for diesel fuel, and as analytical reagents for the determination of certain heavy metals in industrial and natural objects.

Personal contribution of the author. The formulation of the research objectives, performance of the experiments and tests, systematization and generalization of the obtained results were carried out with the direct participation of the author. The results presented in the dissertation were verified and confirmed by the author.

Approbation and application of the research results. A total of 34 scientific works related to the dissertation research have been published, including 1 Azerbaijani patent, 12 scientific articles (7 of which were published abroad), and 21 abstracts presented at international and national conferences. The results of the dissertation research were presented and discussed at the following conferences: the International Scientific Conference on "Actual Problems of Modern Natural and Economic Sciences" (Ganja, 2019, 2021), the XIII International Scientific Conference on "Actual Problems of Chemistry" (Baku, 2019, 2021), the VII and VIII International Scientific and Technical Conferences "Alternative Sources of Raw Materials and Fuel" (Minsk, 2019, 2021), the International Scientific Conference "Actual Problems of Modern Chemistry" (Baku, 2019), the International Scientific Conference "Innovative Development Prospects of Chemical Technology and Engineering" (Sumgait, 2019), the International Conference on Actual Problems of Chemical Engineering APCE 2020 (Baku, 2020), the VIII International Scientific Conference on "Chemistry of Coordination Compounds" (Baku, 2020), the Republican Scientific-Practical Conference "Problems and Development Trends of Modern Chemistry" (Baku, 2020), the Scientific-Practical Conference "Prospects for the Development of Modern Mathematical and Natural Sciences" (Voronezh, 2020), the VIII All-Russian Conference "Current Issues of Chemical Technology and Environmental Protection" (Cheboksary, 2020), the Kyiv Conference on Analytical Chemistry: Modern Trends (Kyiv, 2022), the Republican Scientific Conference of Doctoral Students, Master's Students and Young Researchers on "Chemistry and Chemical Technology" (Baku, 2022), the 7th International Conference "Ecological and Environmental Chemistry–2022" (Chisinau, 2022), the Republican Scientific Conference dedicated to

the 90th anniversary of Academician Nadir Mir-Ibrahim Seyidov on "Catalysts and Olefin-Based Oils" (Baku, 2022), the International Conference "Modern Problems of Theoretical and Experimental Chemistry" dedicated to the 90th anniversary of Academician Rafiga Aliyeva (Baku, 2022), and the Sixth International Scientific Conference "Advances in Synthesis and Complexing" (Moscow, 2022).

Name of the institution where the dissertation research was performed. The dissertation research was carried out at the Y.H. Mammadaliyev Institute of Petrochemical Processes under the Ministry of Science and Education of the Republic of Azerbaijan and at Azerbaijan State Pedagogical University.

Scope of the dissertation. The dissertation consists of 158 pages and includes an introduction (9303 characters), four chapters (Chapter I 68193 characters, Chapter II 16807 characters, Chapter III 55884 characters, Chapter IV 18309 characters, conclusions 2530 characters), a list of 154 references, and a list of abbreviations. The total volume of the dissertation comprises 171026 characters, excluding figures, tables, appendices, and references. The dissertation contains 7 tables and 14 figures.

The introduction presents the relevance and degree of investigation of the topic, the object and subject of the research, the purpose and objectives of the study, research methods, reliability of the results, the main provisions submitted for defense, the scientific novelty of the research, its theoretical and practical significance, the author's personal contribution, as well as the approbation and application of the obtained results.

Chapter I of the dissertation contains the literature review. In accordance with the dissertation topic, this chapter is devoted to the analysis of literature data concerning the synthesis of sterically hindered cycloalkylphenols formed during the alkylation reactions of phenol with cycloolefins and olefins, the synthesis of Mannich reaction bases via aminomethylation reactions of cycloalkylphenols, and their application in the analysis of certain heavy metals. Particular attention in the literature review was paid to the presentation and

critical analysis of research results published during the last decade.

Chapter II of the dissertation is devoted to the methodologies employed for conducting the experiments. This chapter describes the starting materials, their physicochemical properties, the procedures of the performed syntheses, as well as the analytical methods used for the investigation of the reactions and the characterization of the target products formed during the reactions. The results of the scientific investigations were based on measurements carried out using modern analytical instruments.

Chapter III of the dissertation is devoted to the investigation of the aminomethylation reactions of para-cycloalkylphenols, 2-(methylcycloalkyl)-4-methylphenols, phenol, *para*-cresol, and *meta*-cresol with formaldehyde and piperidine. In this chapter, the material balances and elemental compositions of the obtained organic compounds were studied, and modern physicochemical methods, including NMR and IR spectroscopy, were employed for the determination of their chemical structures.

Chapter IV of the dissertation discusses the application areas of piperidinomethylcycloalkylphenols obtained via the amino-methylation reaction. This chapter is devoted to the investigation of the synthesized piperidinomethylcycloalkylphenols as antioxidants for diesel fuel, as ligands in catalytic precursors used in ethylene oligomerization reactions, and to the study of the formation and extraction conditions, as well as the physicochemical properties, of complexes of cobalt(II), iron(III), and copper(II) with sterically hindered aminophenols. Furthermore, new analytical methods enabling the determination of these metals in various objects were developed. In addition, the dissertation includes the conclusions derived from the conducted research, a list of referenced literature sources, appendices, and a list of abbreviations.

THE MAIN CONTENT OF THE RESEARCH

Starting materials, experimental procedures, and analytical methods for product characterization

For the purpose of conducting the investigations, phenol, *p*-cresol, *m*-cresol, *p*-(1-methylcyclohexyl)phenol, *p*-(1-methylcyclopentyl)phenol, *p*-(3-methylcyclohexyl)phenol, *p*-(3-methylcyclohexen-3-yl-isopropyl)phenol, *p*-(4-methylcyclohexen-3-yl-isopropyl)phenol, *p*-[3(4)-methylcyclohexen-3-yl-isopropyl]phenol, 2(1-methylcyclohexyl)-4-methylphenol, 2(1-methylcyclopentyl)-4-methylphenol, 2(3-methylcyclohexyl)-4-methylphenol, 2(3-methylcyclohexen-3-yl-isopropyl)-4-methylphenol, 2(4-methylcyclohexen-3-yl-isopropyl)-4-methylphenol, 2[3(4)-methylcyclohexen-3-yl-isopropyl]-4-methylphenol, piperidine, and a 30% formaldehyde solution (formalin) were used as raw materials for the synthesis of the main products, with benzene and hexane employed as solvents.

p-(1-Methylcyclopentyl)phenol is synthesized via the cycloalkylation reaction of phenol with 1-methylcyclopentene in the presence of KU-23 and an orthophosphoric acid-impregnated Y-type zeolite catalyst. The compound possesses the following physicochemical properties: boiling point 147–148°C/10 mmHg, melting point 88°C, molar mass 176 g/mol. The calculated elemental composition is C = 81.8%, H = 9.1%, while the found values are C = 81.3%, H = 8.7%.

p-(1-Methylcyclohexyl)phenol is synthesized via the cycloalkylation of phenol with 1-methylcyclohexene in the presence of KU-23 and an orthophosphoric acid-impregnated Y-type zeolite catalyst. The compound possesses the following physicochemical properties: boiling point 161–164°C/10 mmHg, melting point 96°C, molar mass 190 g/mol. The calculated elemental composition is C = 82.1%, H = 9.5%, while the found values are C = 81.4%, H = 9.2%.

p-(3-Methylcyclohexen-3-yl-isopropyl)phenol is synthesized via the alkylation of phenol with 1-methyl-3-isopropenylcyclohexen-1-yl (diprene) in the presence of KU-23 and an orthophosphoric acid-impregnated Y-type zeolite catalyst. The compound possesses the following physicochemical properties: boiling point 193–196°C/10

mmHg, melting point 106°C, molar mass 230 g/mol. The calculated elemental composition is C = 83.5%, H = 9.6%, while the found values are C = 83.1%, H = 9.2%.

p-(4-Methylcyclohexen-3-yl-isopropyl)phenol is synthesized via the alkylation of phenol with 1-methyl-4-isopropenylcyclohexen-1-yl (dipentene) in the presence of KU-23 and an orthophosphoric acid-impregnated Y-type zeolite catalyst. The compound possesses the following physicochemical properties: boiling point 198–202°C/10 mmHg, melting point 108°C, molar mass 230 g/mol. The calculated elemental composition is C = 83.5%, H = 9.6%, while the found values are C = 83.1%, H = 8.8%.

p-[3(4)-Methylcyclohexen-3-yl-isopropyl]phenol is synthesized via the alkylation of phenol with a cyclodimer mixture of isoprene (a 160–180°C fraction of diprene and dipentene) in the presence of KU-23 and an orthophosphoric acid-impregnated Y-type zeolite catalyst. The compound possesses the following physicochemical properties: boiling point 190–205°C/10 mmHg, refractive index - n_D^{20} = 1.5450, density - ρ_4^{40} = 0.9145, and molar mass 230 g/mol. The calculated elemental composition is C = 83.5%, H = 9.6%, while the found values are C = 83.3%, H = 9.2%.

2(1-Methylcyclopentyl)-4-methylphenol is synthesized via the cycloalkylation of *p*-cresol with 1-methylcyclopentene in the presence of KU-23 and an orthophosphoric acid-impregnated Y-type zeolite catalyst. The compound possesses the following physicochemical properties: boiling point 158–160°C/10 mmHg, melting point 39°C, molar mass 190 g/mol. The calculated elemental composition is C = 82.1%, H = 9.4%, while the found values are C = 81.6%, H = 9.3%.

2(1-Methylcyclohexyl)-4-methylphenol is synthesized via the cycloalkylation of *p*-cresol with 1-methylcyclohexene in the presence of KU-23 and an orthophosphoric acid-impregnated Y-type zeolite catalyst. The compound possesses the following physicochemical properties: boiling point 170°C/10 mmHg, melting point 45°C, molar

mass 214 g/mol. The calculated elemental composition is C = 82.3%, H = 9.8%, while the found values are C = 82.0%, H = 9.6%.

2(3-Methylcyclohexyl)-4-methylphenol is synthesized via the cycloalkylation of *p*-cresol with 3-methylcyclohexene in the presence of KU-23 and an orthophosphoric acid-impregnated Y-type zeolite catalyst. The compound possesses the following physicochemical properties: boiling point 165°C/10 mmHg, melting point 41°C, molar mass 214 g/mol. The calculated elemental composition is C = 82.3%, H = 9.8%, while the found values are C = 81.6%, H = 9.4%.

2(3-Methylcyclohexen-3-yl-isopropyl)-4-methylphenol is synthesized via the alkylation of *p*-cresol with 1-methyl-3-isopropenylcyclohexen-1-yl (diprene) in the presence of KU-23 and an orthophosphoric acid-impregnated Y-type zeolite catalyst. The compound possesses the following physicochemical properties: boiling point 205–210°C/10 mmHg, refractive index - n_D^{20} = 1.5035, density - ρ_4^{40} = 1.0133, and molar mass 244 g/mol. The calculated elemental composition is C = 83.6%, H = 9.8%, while the found values are C = 83.3%, H = 9.5%.

2(4-Methylcyclohexen-3-yl-isopropyl)-4-methylphenol is synthesized via the alkylation of *p*-cresol with 1-methyl-4-isopropenylcyclohexen-1-yl (dipentene) in the presence of KU-23 and an orthophosphoric acid-impregnated Y-type zeolite catalyst. The compound possesses the following physicochemical properties: boiling point 215–220°C/10 mmHg, refractive index - n_D^{20} = 1.5267, density - ρ_4^{40} = 1.0375, and molar mass 244 g/mol. The calculated elemental composition is C = 83.6%, H = 9.8%, while the found values are C = 83.2%, H = 9.4%.

2[3(4)-Methylcyclohexen-3-yl-isopropyl]-4-methylphenol is synthesized via the alkylation reaction of *p*-cresol with the 160–180°C fraction of isoprene cyclodimers in the presence of KU-23 and an orthophosphoric acid-impregnated Y-type zeolite catalyst. The compound possesses the following physicochemical properties: boiling point 205–220°C/10 mmHg, refractive index - n_D^{20} = 1.5133,

density - ρ_4^{40} = 1.0284, and molar mass 244 g/mol. The calculated elemental composition is C = 83.6%, H = 9.8%, while the found values are C = 83.0%, H = 9.2%.

Phenol (hydroxybenzene) possesses the following physicochemical properties: boiling point 182°C, melting point 43°C, refractive index - n_D^{41} = 1.5426, density - ρ_4^{41} = 1.0576, and molar mass 94 g/mol.

p-Cresol possesses the following physicochemical properties: boiling point 202°C, melting point 35°C, refractive index n_D^{20} = 1.5396, density ρ_4^{20} = 1.0347, and molar mass 108 g/mol.

m-Cresol possesses the following physicochemical properties: boiling point 182°C, melting point 41°C, refractive index n = 1.5426, density ρ = 1.0340, and molar mass 108 g/mol.

Piperidine possesses the following physicochemical properties: boiling point 106°C, melting point 9°C, refractive index n_D^{25} = 1.4530, density ρ_4^{25} = 1.8606, and molar mass 85 g/mol.

Formaldehyde possesses the following physicochemical properties: boiling point −19°C, density 0.8153^{-20}, and molar mass 30 g/mol.

Formalin is a 30% aqueous solution of formaldehyde.

The chromatographic analysis of the reaction products was carried out using an LXM-72 chromatograph.

For the purpose of ascertaining the purity of the synthesized piperidinomethylcycloalkylphenols, thin-layer chromatography was utilized.

The molar masses of the synthesized compounds were evaluated at 200°C employing an MX–1303 mass spectrometer, operating with an ionization voltage of 70 eV and an emission current of 1 mA. Furthermore, a Hewlett-Packard GC/MS chromato-mass spectrometry system was utilized to record the corresponding mass spectra.

The density (ρ) of the synthesized compounds was evaluated via the ASTM D5002 standard on an Anton Paar “DMA 4500M” instrument, while the refractive index (n_D^{20}) was recorded

refractometrically utilizing an “Abbemat 500” refractometer from the same manufacturer. Additionally, the kinematic viscosity values were determined in accordance with the ASTM D445 methodology using an Anton Paar “Stabinger SVM” viscometer.

The chemical structures of the obtained compounds were elucidated via IR spectroscopy on a «Spectrum BX» spectrometer manufactured by «Perkin-Elmer» and an «ALPHA FTIR» spectrometer manufactured by «Bruker» (Germany).

The NMR spectra of the synthesized compounds were recorded on a «Bruker 300» spectrometer operating at 300 MHz, using tetramethylsilane (TMS) as an internal standard.

The elemental analysis of the synthesized compounds was performed using a LECO Europe B.V. analyzer (Geleen, Netherlands) at Laboratory No. 12 of the Institute of Petrochemical Processes under the Ministry of Science and Education of the Republic of Azerbaijan.

Study of aminomethylation reactions of *p*-cycloalkylphenols

The aminomethylation reactions of *p*-methylcycloalkylphenols with piperidine and formaldehyde were carried out under laboratory conditions using a 1:1:1 molar ratio of cycloalkylphenol, piperidine, and formaldehyde. The reactions were performed at 80°C for 2 hours in the presence of benzene as a solvent.

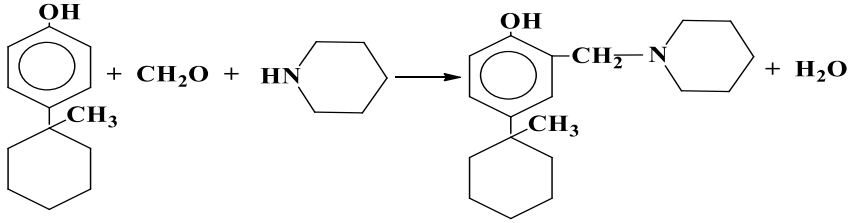
As an example, the results of the aminomethylation reaction of *p*-(1-methylcyclohexyl)phenol with piperidine and formaldehyde are considered.

The aminomethylation reaction was carried out in a three-necked flask charged with 47.5 g (0.25 mol) of *p*-(1-methylcyclohexyl)-phenol, 21.3 g (0.25 mol) of piperidine, and 47.5 g of benzene as solvent (1:1 molar ratio). The mixture was heated with stirring. When the reaction temperature reached 45°C, 7.5 g of formalin was added dropwise into the flask. After the calculated amount of formalin had been added, the reaction temperature was raised to 80°C, and the mixture was further stirred for 2 hours. Subsequently, the temperature

was increased to 110°C to remove the solvent (benzene) and the water formed during the reaction.

The resulting product was cooled to 40°C, washed with water, and then subjected to rectification under reduced pressure (5 mmHg) to isolate 2-piperidinomethyl-4(1-methylcyclohexyl)phenol. The obtained compound was further purified by washing with hexane.

The reaction equation for the aminomethylation of *p*-(1-methylcyclohexyl)phenol with formaldehyde and piperidine is shown below.



Below is the stepwise material balance for the synthesis of 2(piperidinomethyl)-4(1-methylcyclohexyl)phenol.

I. Aminomethylation	mass, g	%
Starting material:		
1) *p*-(1-Methylcyclohexyl)phenol	47.5	62.3
2) Piperidine	21.3	27.9
3) Formalin	7.5	9.8
Total:	76.3	100.0
Obtained:		
Aminophenol + water	75.6	99.1
Loss	0.7	0.9
Total:	76.3	100.0
II. Separation		
Starting material:		
Aminophenol + water mixture	80.0	100.0
Total:	80.0	100.0
Obtained:		
- Aminophenol	71.8	89.8
- water mixture	7.6	9.5

Loss	0.6	0.7
Total:	80.0	100.0

III. Rectification		
Starting material:		
- Aminophenol	71.8	100.0
Total:	71.8	100.0
Obtained:		
1) Recovered piperidine	2.4	6.7
2) Recovered *p*-(1-methylcyclohexyl)phenol	4.8	3.3
3) 2-Piperidinylmethyl-4(1MCYH)phenol	62.1	86.5
4) Residue	1.8	2.5
Loss	0.7	1.0
Total:	71.8	100.0

The analysis of the material balance shows that the reaction produces 62.1 g of 2-piperidinomethyl-4(1-methylcyclohexyl)phenol, representing an 86.5% yield relative to the starting *para*-(1-methylcyclohexyl)phenol.

The IR, ^{1}H and ^{13}C NMR spectra of the synthesized piperidinomethylcyclohexylphenol were characterized and are detailed below.

Figure 1 illustrates the integral curves of the IR spectrum for 2-piperidinomethyl-4(1-methylcyclohexyl)phenol.

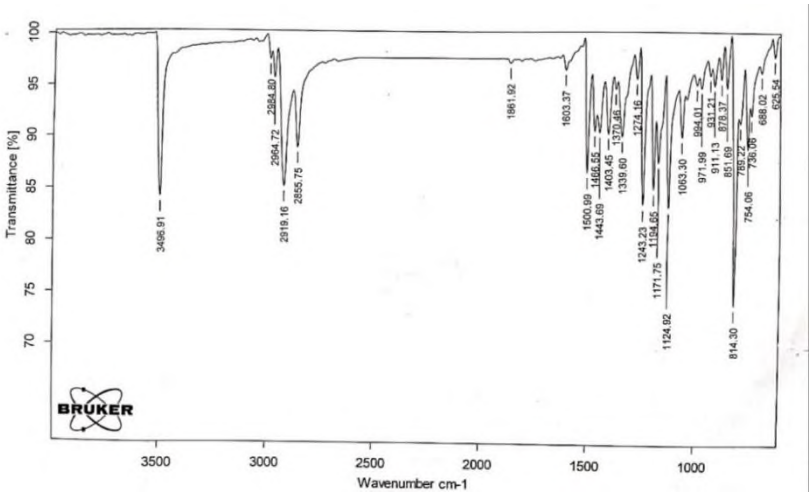


Figure 1. IR spectrum of 2-piperidinomethyl-4(1-methyl-cyclohexyl)phenol.

In the IR spectrum of the synthesized 2-piperidinomethyl-4(1-methylcyclohexyl)phenol, the following characteristic absorption bands are observed: 754 cm^{-1} corresponding to C–H stretching vibrations in the CH_2 group; 1274, 1339, 1370, 1443, 1455, 2855, 2919, and 2964 cm^{-1} corresponding to deformation and stretching vibrations of C–H bonds in CH_2 and CH_3 groups; 814 and 878 cm^{-1} corresponding to a 1,2,4-trisubstituted benzene ring; 1501 cm^{-1} corresponding to benzene ring vibrations; 1603 cm^{-1} corresponding to C=C stretching vibrations of the aromatic ring; 1194 cm^{-1} corresponding to the absorption band of the tertiary nitrogen atom; and 1243 and 3496 cm^{-1} corresponding to deformation and stretching vibrations of the O–H group, respectively.

The integral curves of the ^1H NMR spectrum of 2-piperidinomethyl-4-(1-methylcyclohexyl)phenol are presented in Figure 2. Based on the ^1H NMR integral data, the proton signals can be assigned as follows: the CH_3 group in the cyclohexyl radical appears at δ = 1.37 ppm as a singlet, the cyclohexyl protons are observed in the region δ = 1.76–2.21 ppm, the $N(CH)_2$ group appears at δ = 2.33 ppm as a singlet, the CH_2N protons appear in the

region δ = 3.93–4 ppm as a multiplet, and the aromatic protons are observed at δ = 6.57, 7.13, and 7.27 ppm as multiplets.

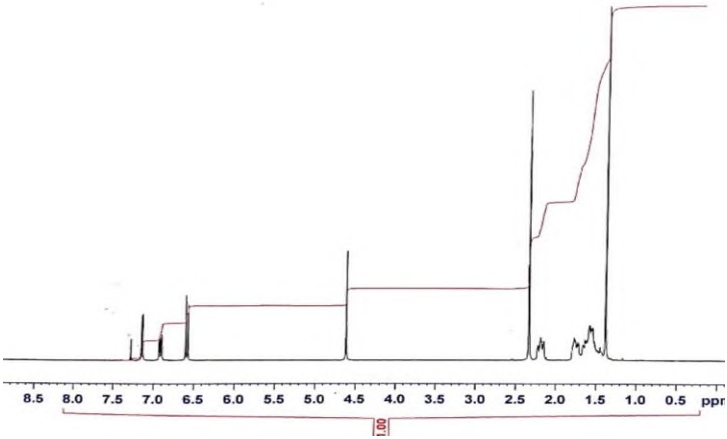


Figure 2. ^{1}H NMR spectrum of 2-piperidinomethyl-4(1-methylcyclohexyl)phenol.

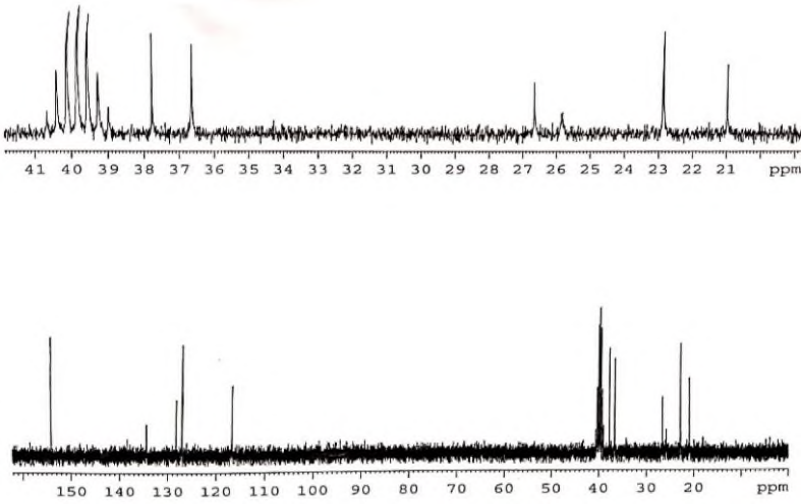


Figure 3. ^{13}C NMR spectrum of 2-piperidinomethyl-4(1-methylcyclohexyl)phenol.

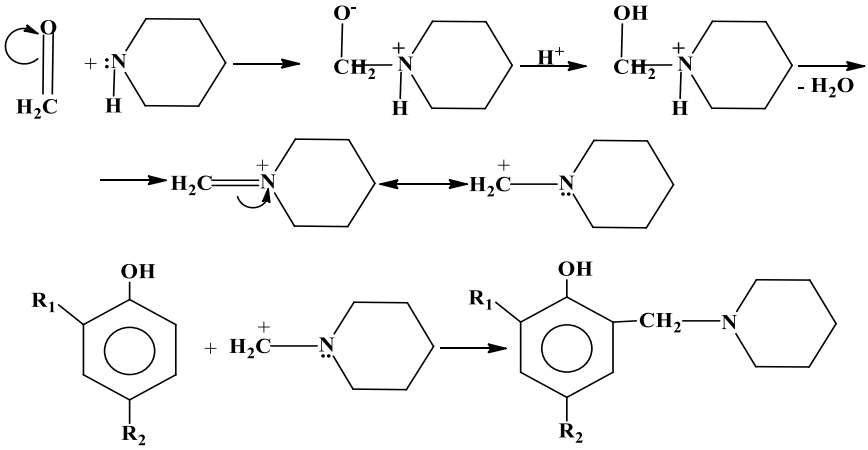
The ^{13}C NMR spectrum of 2-piperidinomethyl-4(1-methyl cyclohexyl)phenol are presented in Figure 3. Based on the ^{13}C NMR

spectral data, the carbon signal of the CH_3 group in the cyclohexyl radical appears at δ = 21 ppm as a singlet, while the carbon atoms of the cyclohexyl group are observed at δ = 26.1, 36.7, and 37.8 ppm as singlets. The carbon atom of the $N(CH_2)_2$ group appears at δ = 40.1 ppm as a singlet. The aromatic ring carbon atoms are observed at δ = 117, 127.5, 128, 135, and 154 ppm as singlets.

The integral curves of the IR, ^1H NMR, and ^{13}C NMR spectra of 2-piperidinomethyl-4(1-methylcyclohexyl)phenol confirm the complete elucidation of its chemical structure.

The physicochemical properties and elemental compositions of 2-piperidinomethyl-4(methylcycloalkyl)phenols are presented in Table 1.

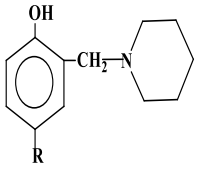
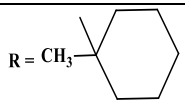
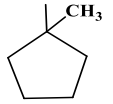
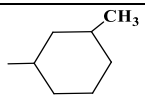
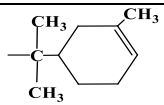
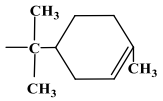
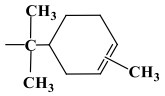
The general mechanism of the aminomethylation reactions of sterically hindered phenols with piperidine and formaldehyde is illustrated in the following scheme:



When **R_1= H, R_2= cycloalkyl;**
When **R_1= cycloalkyl, R_2= CH_3.**

Table 1

Physicochemical properties and elemental composition of 2-piperidinomethyl-4(methylcycloalkyl)phenols

	Boiling Point, °C/ 5 mmHg	Melting Point, °C /Refractive Index /Density	Molar Mass	Calculated / Found, %		
				C	**H**	**N**
	167-170	78	287	79.4 / 78.8	10.1 / 9.7	4.9 / 4.4
	156-158	63	273	79.1 / 78.6	9.9 / 9.5	5.1 / 4.5
	161-163	72	287	79.4 / 78.7	10.1 / 9.6	4.9 / 4.6
	194-197	n_D^{20} -1,5365 ρ_4^{40} -0.9280	327	80.7 / 80.2	10.1 / 9.4	4.3 / 3.9
	202-207	n_D^{20} -1,5436 ρ_4^{40} -0.9517	327	80.7 / 79.6	10.1 / 9.2	4.3 / 3.7
	194-210	n_D^{20} -1,5472 ρ_4^{40} -0.9405	327	80.7 / 79.2	10.1 / 9.0	4.3 / 4.1

The condensation reaction of a compound containing an active (mobile) hydrogen atom with a secondary amine and formaldehyde is carried out to yield an α-aminocarbinol as an intermediate. In the initial stage, the interaction between the amine and formaldehyde generates a carbocation (iminium ion), which subsequently attacks the

compound containing the active hydrogen atom. Driven by the lone pair of electrons, the initial nucleophilic attack of the nitrogen atom is directed toward the carbonyl group of the aldehyde, followed by the elimination of a water molecule to form the cationic species. Ultimately, this carbocation attacks the ortho-position of the cycloalkylphenol possessing the active hydrogen atom, leading to the formation of the corresponding Mannich base.

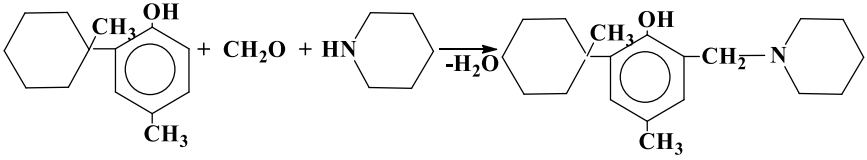
Study of the aminomethylation of 2(methylcycloalkyl)-4-methylphenols using piperidine

The aminomethylation reactions of 2(1-methylcycloalkyl)-4-methylphenols were carried out using piperidine and formaldehyde, with benzene as the solvent.

As an example, the results of the aminomethylation reaction of 2(1-methylcyclohexyl)-4-methylphenol with piperidine and formaldehyde are considered below.

For the aminomethylation reaction, 40.8 g (0.2 mol) of 2(1-methylcyclohexyl)-4-methylphenol, 40.8 g of solvent (benzene), and 17.0 g (0.2 mol) of piperidine were placed in a three-necked flask and heated. The study was then continued following the procedure described above.

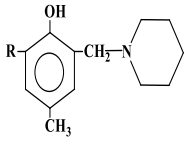
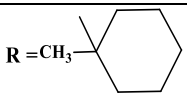
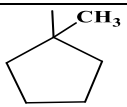
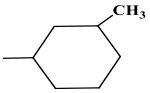
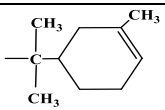
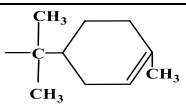
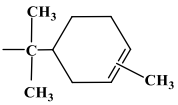
The reaction scheme of the aminomethylation of 2(1-methylcyclohexyl)-4-methylphenol with piperidine is shown below.



The synthesized 2(1-methylcyclohexyl)-4-methyl-6(piperidinomethyl)phenol was characterized by IR, ^{1}H and ^{13}C NMR spectral analyses, and its data were found to be in good agreement with those of 2-piperidinylmethyl-4(1-methylcyclohexyl)phenol presented above. The physicochemical properties and elemental compositions of 2(methylcycloalkyl)-4-methyl-6-piperidinomethylphenols are given in Table 2

Table 2

Physical and chemical properties and elemental compositions of 2(methylcycloalkyl)-4-methyl-6-piperidinomethylphenols

	Boiling Point, °C/ 5 mmHg	Melting Point, °C /Refractive Index /Density	Molar mass, g/mol	Calculated / Found, %		
				C	**H**	**N**
	191-193	45	301	79.7 / 78.8	10.7 / 9.4	4.7 / 4.3
	168-171	38	287	79.4 / 78.2	10.1 / 9.5	4.9 / 4.1
	182-186	41	301	79.7 / 78.6	10.7 / 9.0	4.7 / 4.1
	207-212	n_D^{20} - 1,5513 ρ_4^{40} - 0.9447	341	80.9 / 80.4	10.3 / 9.6	4.1 / 3.5
	214-217	n_D^{20} - 1,5738 ρ_4^{40} - 0.9608	341	80.9 / 80.1	10.3 / 9.1	4.1 / 3.0
	205-217	n_D^{20} - 1,5652 ρ_4^{40} - 0.9529	341	80.9 / 79.6	10.3 / 8.8	4.1 / 3.2

Based on the prepared material balance, 47.5 g of 2(1-methylcyclohexyl)-4-methyl-6-piperidinomethylphenol was obtained, corresponding to a yield of 78.9% calculated with respect to the starting material, 2(1-methylcyclohexyl)-4-methylphenol.

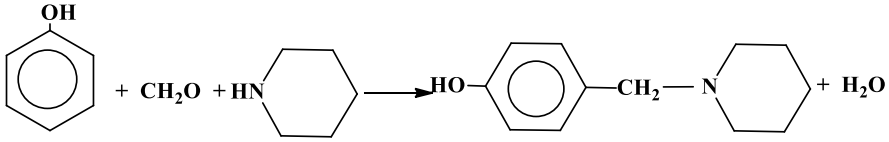
Aminomethylation reactions of phenol, *p*- and *m*-cresols with piperidine

Phenol, *p*- and *m*-cresols, piperidine, and formaldehyde were used as starting materials, with benzene employed as the solvent.

As an example, the results of the aminomethylation reaction of phenol with piperidine and formaldehyde are considered.

For the reaction, 23.5 g (0.25 mol) of phenol, 23.5 g of solvent (benzene), and 21.3 g (0.25 mol) of piperidine were placed in a three-necked flask and heated. Further investigations were carried out following the procedure described above.

The aminomethylation reaction of phenol with piperidine proceeds according to the following equation:



The synthesized 4-piperidinylmethylphenol was characterized by IR, ^{1}H and ^{13}C NMR spectral analyses, and its data were found to be in good agreement with those of 2-piperidinylmethyl-4(1-methylcyclohexyl)phenol presented above.

Based on the material balance, 31.3 g of 4-piperidinylmethyl-phenol was obtained, corresponding to a yield of 77.7% calculated with respect to phenol used as the starting material.

Similarly, the aminomethylation reactions of *p*- and *m*-cresols with formaldehyde and piperidine were carried out, affording the corresponding Mannich bases.

Study of the applications of piperidinylmethylcycloalkylphenols

Piperidinylmethylcycloalkylphenols were tested as ligands for catalytic precursors used in ethylene oligomerization reactions, as antioxidants in diesel fuel, and as reagents for the determination of Cu(II), Co(II), and Fe(III) ions.

Evaluation of piperidinylmethylcycloalkylphenols as ligands in catalytic precursors for ethylene oligomerization processes

Based on the conducted studies, new catalysts for ethylene oligomerization were synthesized via the interaction of the obtained 2(piperidinylmethyl)-4-cycloalkylphenols with $ZrCl_4$.

It was established that the oligomerization products of ethylene obtained using heterogenized zirconium complexes formed by the addition of 2(piperidinylmethyl)-4-cycloalkylphenols, in the presence of the cocatalyst $(C_2H_5)_2AlCl$, consist predominantly of a C_4 – C_{10} fraction of linear α-olefins. The yield of oligomer products was found to depend on the reaction pathway and ligand structure, ranging from 80–90%.

The zirconium complex obtained from the reaction with 2(piperidinylmethyl)-4(1-methylcyclohexyl)phenol, together with the cocatalyst $(C_2H_5)AlCl_2$, was used for ethylene oligomerization in aliphatic solvents (hexane, isooctane, heptane, etc.) at 90°C and 1.8–5.0 MPa, with an Al:Zr molar ratio of (25–30):1. Under these conditions, ethylene was converted into a polyethylene oil fraction. The yield based on converted ethylene was 63.4–69.0%.

When 2(piperidinylmethyl)-4-methylcycloalkylphenols are used as ligands in the synthesis of catalysts for ethylene oligomerization, a higher yield of the target products (C_4–C_{10} olefins) of 88–91% is observed. In comparison, the use of known catalysts reported in the literature provides yields of 70–75%.

As a final conclusion, it can be stated that 2(piperidinylmethyl)-4-methylcycloalkylphenols can be effectively used as ligands in catalytic precursors applied in ethylene oligomerization reactions.

Evaluation of 2-piperidinylmethyl-4[1(3)-methyl-cycloalkyl]phenols as antioxidants in diesel fuel

The synthesized 2-piperidinylmethyl-4(1-methylcyclopentyl)-phenol, 2-piperidinylmethyl-4(1-methylcyclohexyl)phenol, and 2-piperidinylmethyl-4(3-methylcyclohexyl)phenol were tested as antioxidants in diesel fuel (DF) in accordance with GOST 305-2013.

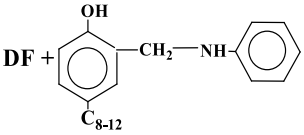
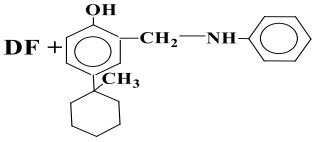
The results of the study showed that the presence of a piperidine moiety, hydroxyl group, cycloolefin fragment, and aromatic ring in the structure of the obtained antioxidants facilitates their solubility in fuels, which in turn leads to an improvement in fuel quality characteristics.

The proposed antioxidants for diesel fuel 2-piperidinylmethyl-4(1-methylcyclopentyl)phenol, 2-piperidinylmethyl-4(1-methylcyclohexyl)phenol, and 2-piperidinylmethyl-4(3-methylcyclohexyl) phenol were synthesized by the methods described above.

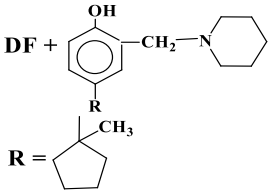
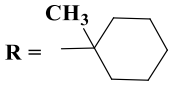
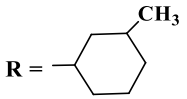
Fuel samples were prepared by adding the investigated and reference antioxidants to diesel fuel at a concentration of 0.004%. The oxidation stability of both additive-free and antioxidant-containing samples was evaluated after 4 hours of oxidation at 120°C by determining the amount of sediment formed in the diesel fuel. The results of the experiments are presented in Table 3.

Table 3

Results of testing 2-piperidinylmethyl-4-methylcycloalkyl-phenols as antioxidants in diesel fuel

N	Antioxidants	AO content, %	Sediment content, mg/100 cm³
1	**2**	**3**	**4**
1.	DF (without AO addition)	-	4.35
2.	DF + ionol	0.004	1.0
3.	 (known)	0.004	0.9
4.	 (known)	0.004	0.7

Continuation of Table 3

1	2	3	4
5		0.004	0.2
6.		0.004	0
7.		0.004	0

As can be seen from Table 3, compared with known antioxidants, the addition of the proposed piperidinylmethylcycloalkylphenols to diesel fuel results in a slight sediment formation (0.2 mg/100 cm³) for sample (5), whereas no sediment formation is observed for samples (6) and (7).

Thus, the synthesized 2-piperidinylmethyl-4-methylcycloalkylphenols can be recommended as antioxidants for use in diesel fuel.

Study of the determination of copper(II), iron(III), and cobalt(II) using piperidinylmethylcycloalkylphenols in natural and industrial samples

Methods for the determination of copper, iron, and cobalt as complex compounds with piperidinylmethylcycloalkylphenols were compared and subsequently applied to their determination in natural and industrial samples. For this purpose, piperidinylmethylcycloalkylphenols (AP) were used as organic reagents: 2-piperidinylmethyl-4(1-methylcyclopentyl)phenol (AP_1), 2-piperidinylmethyl-4(1-methylcyclohexyl)phenol (AP_2), 2-piperidinylmethyl-4(3-methylcyclohexyl)phenol (AP_3), 2(3-methylcyclohexyl)-4-methyl-6(pi-

peridinylmethyl)phenol (AP_4), 2-piperidinylmethyl-4-methylphenol (AP_5), and 2-piperidinylmethyl-5-methylphenol (AP_6).

Evaluation of sterically hindered piperidinylmethylcycloalkylphenols as ligands for the determination of Cu(II), Fe(III), and Co(II) ions

Determination of copper in bean samples. A 10 g bean sample was crushed in a porcelain dish and initially dried at 65–75°C, followed by drying at 110°C. After the muffle furnace was heated to 500°C, the dried sample was placed inside for ashing. The resulting ash was dissolved using 0.1 N HNO_3 solution and then filtered into a 100 mL volumetric flask.

The determination of copper was carried out from an aliquot portion placed into an extraction vessel, following the corresponding analytical procedures. The results are presented in Table 4.

Table 4
Results of copper determination in food samples based on piperidinylmethylcycloalkylphenols (μg/kg)

Compound	Analyte	AP	$\overline{X} \pm \frac{t_P S}{\sqrt{n}}$	Pb-DEDTC	$\overline{X} \pm \frac{t_P S}{\sqrt{n}}$
Cu-AP_1	Bean	5.41	5.41±0.49	5.38	5.38±0.55
Cu-AP_2	Bean	5.44	5.44±0.12	5.43	5.43±0.13
Cu-AP_4	Bean	5.47	5.47±0.15	5.36	5.36±0.13

Table 4 presents the results of copper determination in bean samples based on piperidinomethylcycloalkylphenols (AP_1, AP_2, and AP_4). The amount of copper determined via Cu–AP_1, Cu–AP_2, and Cu–AP_4 complexes varies within the range of 5.41–5.47 μg/kg. A close agreement is observed between the results obtained for the analyzed samples and those determined using the Pb–DEDTC-based method. The low values of the standard deviation (±0.12–0.55 μg/kg)

indicate the high repeatability and accuracy of the proposed methodology.

Determination of iron content in fruit. Initially, to decompose the organic compounds present in the fruit, 250 g of dried fruit sample was placed in a muffle furnace preheated to 550–750 °C and incinerated. Following the ashing process, the resulting ash was cooled down and subsequently dissolved in 20 mL of a HCl+HNO3 (3:1) mixture. The obtained mixture was diluted with 50 mL of distilled water and filtered into a 100 mL volumetric flask. Iron determination was performed using an aliquot part according to the relevant standard procedures. The results are presented in Table 5.

Table 5

Results of the determination of iron in natural samples using piperidinomethylcycloalkylphenols (μg/kg)

Experimental Procedure	Analyzed Sample	Amount Added, μg	Detected, μg	$\overline{X} \pm \frac{t_P S}{\sqrt{n}}$
AP_1	Aple	15.0	23.3	23.3±0.71
AP_2	White Cherry	10.0	13.50	13.50±0.30
AP_5	Strawberry	5.0	5.16	5.16±0.14

Table 5 presents the results of iron determination based on piperidinomethylcycloalkylphenols in various fruit samples (apple, white cherry, and strawberry). A close agreement between the added and found amounts of Fe(III) was observed. The low values of the standard deviations (±0.14–0.71 μg/kg), calculated from the obtained results, confirm the high accuracy of the proposed method. In particular, the sensitivity of the method was maintained even for low-concentration samples (strawberry, 5.0 μg).

Determination of cobalt in standard soil samples. Initially, 8 g of the standard soil sample was dissolved in a graphite crucible using

a mixture of 15 mL HF and 5 mL HNO_3 at 50–70°C. In order to remove the excess amount of HF from the resulting solution, 8–9 mL of HNO_3 was added again to the mixture (Table 6).

Table 6

Results of the determination of cobalt in standard soil samples

Compound	Analyzed Sample	Certified Value, Me (%)	Co Found, %
AP_1	Soil ST-1A	0.0046	4.622×10^{-3}
AP_2	Soil SGD-1A	0.0040	4.092×10^{-3}
AP_3	Soil SGKh-3	0.0030	2.996×10^{-3}

Table 6 presents the results of cobalt determination in standard soil samples using piperidinomethylcycloalkylphenols. A high agreement was observed between the certified (passport) values and the determined Co contents. The obtained results, at the 10^{-3} level, demonstrate the applicability of the proposed method for the determination of trace amounts. The systematic nature of the results obtained for different AF compounds confirms the reproducibility and reliability of the developed methodology.

The conducted studies demonstrate that piperidinomethylcycloalkylphenols, based on the formation of complexes with Cu(II), Fe(III), and Co(II) ions, can be effectively used for the development of analytical methods for the determination of metal ions in real samples of various origins. These methods are characterized by simple instrumentation, high selectivity, and satisfactory accuracy, and therefore have broad potential for application in environmental, industrial, and food analysis.

CONCLUSIONS

1. Aminomethylation reactions of *para*-(1-methylcyclohexyl)-, *para*-(1-methylcyclopentyl)-, *para*-(3-methylcyclohexyl)-, *para*-(3-methylcyclohexen-3-yl-isopropyl)-, *para*-(4-methylcyclohexen-3-yl-isopropyl)-, and *para*-[3(4)-methylcyclohexen-3-yl-isopropyl] phenols with formaldehyde and piperidine were investigated. It was established that under conditions of a 1:1:1 molar ratio of cycloalkylphenols, piperidine, and formaldehyde, at 80°C for 2 hours, aminomethylation proceeds with yields of 57.6–86.5% (calculated relative to the initial para-methylcycloalkylphenol), leading to the formation of 2-piperidinomethyl-4(methylcycloalkyl)phenols [2, 15, 16, 17, 20, 32, 31, 33].

2. The synthesis of aminomethyl derivatives based on formaldehyde and piperidine with 2-(methylcycloalkyl)-4-methylphenols was carried out. It was established that, under optimal conditions of the aminomethylation reactions, the yields of the Mannich bases 2(methylcycloalkyl)-4-methyl-6(piperidinomethyl)phenols range from 58.2 to 78.9% relative to the initial 2-(methylcycloalkyl)-4-methylphenols [11, 13, 22, 29].

3. The reactions of phenol and para- and meta-cresols with formaldehyde and piperidine were carried out. It was found that the yields of the target products obtained via aminomethylation reactions range from 60.8 to 77.7% [14, 21, 25].

4. The stepwise material balances of the investigated aminomethylation reactions were calculated. The chemical structures of the obtained Mannich bases were confirmed, and their physicochemical properties and elemental compositions were determined [23].

5. The compounds obtained from reactions of 2(piperidinomethyl)-4-cycloalkylphenols with $ZrCl_4$ were investigated as ligands in catalytic systems used for ethylene oligomerization reactions, acting as one of the components of heterogeneous metal-complex catalysts at different molar ratios. It was established that when 2(piperidinomethyl)-4-cycloalkylphenols are used as ligands in

catalysts for ethylene oligomerization, the yield of the target products (C_4–C_{10} fraction) increases to 88–91%, whereas the use of conventional catalysts results in yields of 70–75% [34].

6. The synthesized 2-piperidinomethyl-4[1(3)-methylcycloalkyl]phenols were tested as antioxidants in diesel fuel in accordance with GOST 305-2013. The antioxidant performance was evaluated based on the amount of precipitate formed in diesel fuel at 120°C over 4 hours using the LSART apparatus. It was established that no sediment formation occurs after oxidation when 0.004% of 2-piperidinomethyl-4-methylcycloalkylphenols is added to diesel fuel [28].

7. Sterically hindered piperidinomethylcycloalkylphenols were used as complex-forming ligands for the determination of Co(II), Fe(III), and Cu(II) ions in the composition of various samples [1, 3, 4, 5, 6, 7, 8, 9, 10, 12, 18, 19, 24, 26, 27, 30].

THE RESEARCH PRESENTED IN THE DISSERTATION HAS BEEN PUBLISHED IN THE FOLLOWING SCIENTIFIC SOURCES

1. Huseynova, G.A., Zalov, A.Z., Rasulov, Ch.K. Synthesis and investigation of the properties of 2-morpholino(piperidino)methyl-4-methyl-6-(1(3)-methylcycloalkylphenols // Proceedings of the International Scientific Conference "Actual Problems of Modern Natural and Economic Sciences", − Ganja: − 3–4 May,− 2019.− pp. 218–220.

2. Huseynova, G.A., Rasulov, Ch.K., Zalov, A.Z. Aminomethylation reactions of sterically hindered cycloalkylphenols with piperidine // Proceedings of the XIII International Scientific Conference on "Current Problems of Chemistry",− Baku: − May 15–16,− 2019.− pp. 121–122.

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