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SOME PECULİARİTİES OF P-[1(3)-METHYLCYCLOALKYL]PHENOLS INTERACTION REACTIONS WITH PIPERIDINE

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Abstract: *The article explores the synthesis of 2-piperidinomethyl-4-methylcycloalkylphenols as a result of aminomethylation reactions of p-[1(3)-methylcycloalkyl]phenols obtained by catalytic cycloalkylation reactions of phenol and 1-methylcyclopentene, 1- and 3-methylcyclohexenes with piperidine. Aminomethylation reactions were carried out through the interaction of p-cycloalkylphenols with 30% of formaldehyde and piperidine in the presence of a solvent. The reaction was realized at 30℃ for 2 hours. Following results of the studies, it revealed that yields of the obtained target products amounted to 68.8-75.6% on p-(methylcycloalkyl). Chemical structures of 2-piperidinomethyl-4-methylcycloalkylphenols were confirmed by IR, ^{1}H and ^{13}C NMR spectroscopies, and physicochemical properties determined as well.*

Keywords: *phenol, 1(3)-methylcycloalkenes, cycloalkylation, p-[1(3)-methylcycloalkyl]-phenols, piperidine, aminomethylation, 2-piperidinomethyl-4-methylcycloalkyl-phenols*

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Introduction

Last decade's research into literary sources shows that alkylphenols-based chemical additives are widely used in different areas of industry [1-5]. In particular, they are used as antioxidants, additives, stabilizers, oxygenators of high efficiencies for oils, fuels, polymer materials, simultaneously with a ligand for catalytic precursors in olefins oligomerization processes, medicinal preparations to fight plant diseases; as pesticides in agriculture [6-11].

The article deals with the synthesis of 2-piperidinomethyl-4-methylcycloalkylphenols by aminomethylation reactions of p-[1(3)-methylcycloalkyl]-phenols obtained due to catalytic cycloalkylation reactions of phenol with 1-methylcyclopentene (1-MCP), 1-methylcyclohexene (1-MCH) and 3-methylcyclohexene (3-MCH) with piperidine.

Experimental part

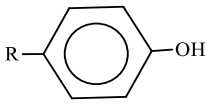
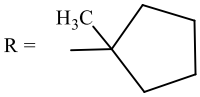
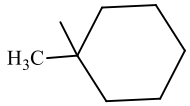
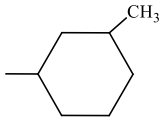
p-(1-Methylcyclopentyl)phenol, p-(1-methylcyclohexyl)phenol, p-(3-methylcyclohexyl)phenol, formaline and piperidine have been used as primary raw materials in aminomethylation reactions.

p-[1(3)-Methylcycloalkyl]phenols were obtained by catalytic cycloalkylation of phenol with 1-methylcyclopentene, 1- and 3-methylcyclohexenes [12, 13] and their physicochemical properties as shown in Table 1.

Chromatographic analysis of the p-(methylcycloalkyl) phenols used for the reaction was carried out using LXM-72 chromatograph.

Chromatographic analyses of the reaction and rectification products were realized on LXM-72M chromatograph. The column length was 2 m, 0.2±0.25 mm of the chromatone N-AW-/JMC silanated with dimethylchlorosilane washed by an acid was taken as a solid carrier, 5% of SE-30 methylcyloxane elastomer - as an inactive phase. The column initial temperature was 50°C, final temperature - 280 °C, programming rate - 10 °C/min., helium gas rate - 50 ml/min., evaporator temperature - 355°C, detector temperature - 300°C, diagramme tape rate – 60 mm/h.

Table 1. Physicochemical properties of p-[1(3)-methylcycloalkyl]phenols

N		Boiling point, °C/mm Hg	Melting point, °C	Mol. mass	Elemental composition, %			
					Calc.		Found	
					C	H	C	H
1.		147-148	88	176	81.8	9.1	81.8	9.2
2.		161-164	96	190	82.1	9.5	82.4	9.7
3.		158-160	91	190	82.1	9.5	82.7	10.0

Piperidine boiling point - 106 ℃; n_D^{20} -1.4530; ρ_4^{20} -0.861; molecular mass-85.

In both cases, total 100% of the general peaks areas were taken for calculation of the amount of the initial and final products compositions by percent.

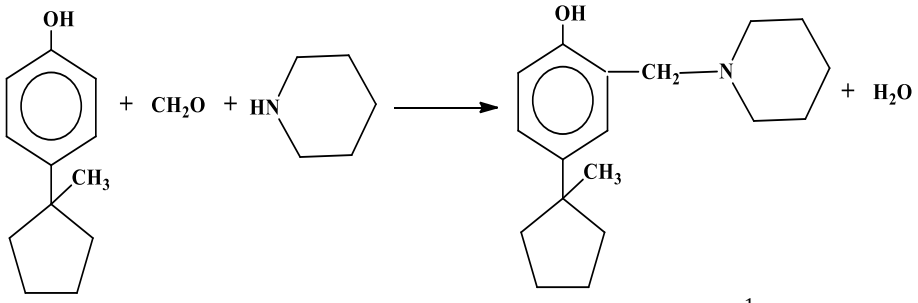
Aminomethylation reactions of p-methylcycloalkylphenols with formaldehyde and piperidine were studied in a three-necked flask. Calculated amounts of p-methylcycloalkylphenol, piperidine and the solvent (benzene) were added to the flask and heated. 30% formaline in a certain amount was added to the flask through dropping funnel within 45 min. when the temperature reached 30°C. Formaline addition was followed by increasing temperature up to 80°C and stirring for further 2 hours. At the end of the reaction, the mixture was washed by water for releasing unreacted formaldehyde. The amine compound was converted into the acid salt for purifying from alkylphenol. Then, the amine was treated by solid NH_4 – an aqueous solution of acid salt and free amine compound was extracted. The amine obtained was released from water by means of extraction. After purification from benzene, the residue was rectified at low pressure; the obtained 2-piperidinomethyl-4-methylcycloalkylphenols chemical structures and physicochemical properties were determined.

The reaction products spectra were drawn on ALPHA IR-Furye spectrometer of "BRUKER" company in the range of 600-4000 cm^{-1} on Se/Zn crystal.

NMR spectra of the compounds obtained were drawn in NMR spectrometer (AFR) of 300 mHs speed. Chemical shifts of the signals (ppm) were taken in comparison to tetramethylsilane. Relative compositions of the protons of different structural fragments were determined by integration of peak areas on appropriate bands of spectra.

Synthesis of 2-piperidinomethyl-4)1-methylcyclopentyl-phenol

The equation of p-(1-methylcyclopentyl)phenol aminomethylation reaction with formaldehyde and piperidine is given below:



A flask was filled with 44.0 g (0.25 mol) of p-(1-methylcyclopentyl)phenol, 7.5 g (0.25 mol) of formaldehyde, 44.0 g of benzene and heated. 21.3 g (0.25 mol) of piperidine was added to the mixture at 40°C by drops. After the addition of piperidine, temperature was raised up to 80°C and stirred within 2 hours. Then, the mixture was released from benzene, water and unreacted formaldehyde. The reaction residue underwent rectification in a Claisen flask, the target product was separated and its physicochemical properties and chemical structure determined.

42.5 g of 2-piperidinomethyl-4(1-methylcyclopentyl)phenol was obtained as a result of rectification and proved 72.4% of the the yield amount.

IR and ^{1}H NMR spectra of the synthesized 2-piperidinomethyl-4(1-methylcyclopentyl)phenol were drawn. Results of IR, ^{1}H and ^{13}C NMR spectra of the substance are presented below.

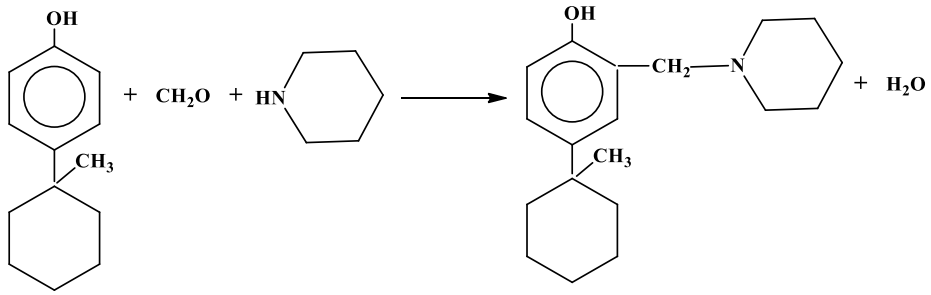
The following absorption bands were observed on IR spectrum of the sample: mathematical vibration of C-H bond of CH_2 group at 745 cm^{-1}; deformation and valence vibrations of C-H bond of CH_2 and CH_3 groups additionally at 1313, 1362, 1383, 1454, 1477, 2869, 2929, 2954 cm^{-1}; 1,2,4-substituted benzene nucleus at 818, 873 cm^{-1}, benzene ring at 1503 cm^{-1}; C=C bond of benzene nucleus at 1619 cm^{-1}; =C−H bond at 1619 cm^{-1}; absorption band of tert-nitrogen atom at 1193 cm^{-1}, C− O− C bond at 1097, 1123 cm^{-1}; deformation and valence bonds referring to OH group O-H bond at 1248, 3291, 3370 cm^{-1}.

The following absorption signals are observed on NMR ^{1}H spectrum of 2-piperidinomethyl-4(1-methylcyclopentyl)phenol: proton in CH_2 group of cyclopentyl radical at δ=1.45 ppm (in a singlet state), hydrogens in cyclopentyl group at δ=1.6-1.9, hydrogens in $N(CH_2)_2$ group at δ=2.5 (in singlet states), protons in $O(CH_2)_2$ and CH_2N group at δ=3.62-3.7 (in multiplet states), and protons in aromatic nucleus at δ=6.75-7.2 (in multiplet states).

The following absorption signals are observed on NMR ^{13}C spectrum of 2-piperidinomethyl-4(1-methylcyclopentyl)phenol: carbon atoms in CH_3 group at δ=25 ppm (in singlet states), carbon atoms in cyclopentyl group at δ = 27 ppm, in $N(CH_2)_2$ group at δ=52-61.5 ppm (in singlet states), carbon atoms in CH_2N group at δ=59 ppm (in singlet states), in $O(CH_2)_2$ group δ=67.5 ppm (in singlet states), and carbon atoms in aromatic nucleus at δ=115, 122, 126.5, 130, 141.5, 155.5 ppm (in singlet states).

Synthesis of 2-piperidinomethyl-4(1-methylcyclohexyl)phenol

The aminomethylation reaction runs on the equation below:



A flask was filled with 47.5 g (0.25 mol) of p-(1-methylcyclohexyl)phenol, 7.5 g (0.25 mol) of formaldehyde and 47.5 of benzene and heated. 21.3 g (0.25 mol) piperidine was added to the mixture by drops at 40°C. After addition of piperidine, temperature rose up to 80°C and the mixture was stirred within 2 hours at this temperature. Then, the mixture was processed in line with the above-mentioned methodics and underwent rectification.

54.3 g of 2-piperidinomethyl-4(1-methylcyclohexyl)phenol was obtained as a result of rectification and revealed that the yield of the target product amounted to 75.6% on the taken p-(1-methylcyclohexyl)phenol.

Physicochemical properties and chemical structures of the synthesized 2-piperidinomethyl-4(1-methylcyclohexyl)phenol were determined.

Results of IR, ^{1}H and ^{13}C NMR spectral analyses of the substance are given below.

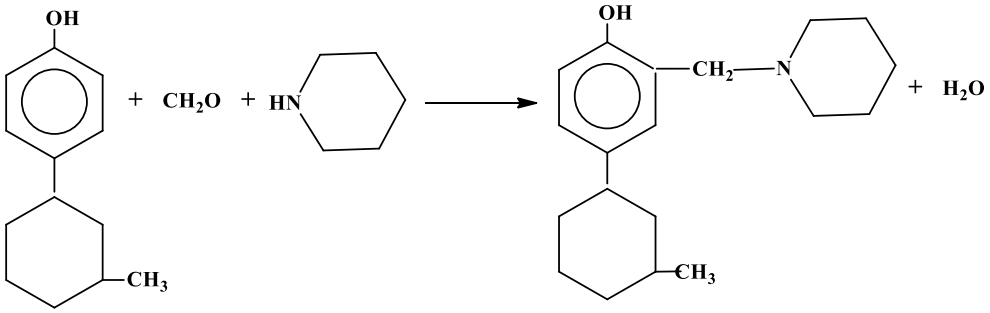
The following absorption bands were observed on IR spectrum of 2-piperidinomethyl-4(1-methylcyclohexyl)phenol: mathematical vibration of CH_2 group C-H bond at 746 cm^{-1}, deformation and valence vibrations of C-H bond of CH_2 and CH_3 groups, at 1313, 1362, 1383, 1454, 2868, 2928, 2953 cm^{-1}, correspondingly; 1,2,4-substituted benzene nucleus at 818, 873 cm^{-1}; benzene ring at 1503 cm^{-1}; C=C bond of benzene nucleus at 1615 cm^{-1}; deformation and valence vibrations of OH group O-H bond at 1192 cm^{-1} referring to tertiary nitrogen atom.

The following absorption bands were observed on NMR ^{1}H spectrum of 2-piperidinomethyl-4(1-methylcyclohexyl)phenol: hydrogen in CH_3 group of cyclopentyl radical at δ= 1.42 ppm (in a singlet state), hydrogens in cyclohexyl group at δ=1.75-2.24 ppm, hydrogens in $N(CH_2)_2$ group at δ=2.84 ppm (in singlet states), $O(CH_2)_2$ and CH_2N (in multiplet states), hydrogen atoms in aromatic nucleus at δ=6.95, 7.12 and 7.39 ppm (in multiplet states).

The following absorption signals were recorded on NMR ^{13}C spectrum of 2-piperidinomethyl-4(1-methylcyclohexyl)phenol: carbon atom in CH_3 group at δ=26, 30.4, 36.4, 37 ppm, in $N(CH_2)_2$ group at δ=51.7 ppm (in a singlet state), carbon atom in CH_2N group at δ=61.8 ppm (in a singlet state), carbon atoms in $O(CH_2)_2$ group at δ=65 ppm (in singlet states), and carbon atoms in aromatic nucleus at δ=115, 119.5, 124, 125, 139, 154 ppm (in singlet states).

Synthesis of 2-piperidinomethyl-4(3-methylcyclohexyl)phenol

P-(3-methylcyclohexyl)phenol aminomethylation reaction with formaldehyde and piperidine is shown in the equation below:



The quantities of the primary components taken for aminomethylation reaction – p-(3-methylcyclohexyl)phenol, formaldehyde and piperidine and the reaction conditions were consistent with quantities of primary components and reaction conditions of the previous experiment.

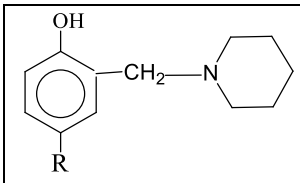
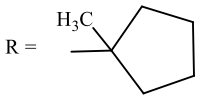
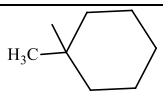
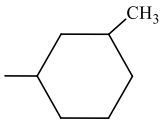
It resulted in obtaining 49.4 g of 2-piperidinomethyl-4(3-methylcyclohexyl) phenol and 68.8% of the target product yield in the (3-methylcyclohexyl) phenol.

Chemical structure, physicochemical properties of the synthesized 2-piperidinomethyl-4(3-methylcyclohexyl)phenol were found out. It revealed that integral curves of the substance IR, ^{1}H and ^{13}C NMR spectra were consistent with previously presented integral curves of 2-piperidinomethyl-4(3-ethylcyclohexyl)phenol.

Physicochemical properties of the

synthesized 2-piperidinomethyl-4[1(3)-methylcycloalkyl]phenols are shown in Table 2.

Table 2. Physicochemical properties of 2-piperidinomethyl-4[1(3)-methylcycloalkyl]phenols

	Boiling point, ^{0}C/mm Hg	Melting point, ^{0}C	Mol.mass	Elemental composition, %					
				Calc.			Found		
				C	H	N	C	H	N
	168-171	63	273	79.1	9.9	5.1	78.6	9.5	4.5
	191-193	78	287	79.4	10.1	4.9	78.8	9.7	4.4
	182-186	72	287	79.4	10.1	4.9	78.7	9.6	4.6

As is evident from Table, calculated mol masses and elemental compositions of synthesized 2-piperidinomethyl-4[1(3)-methylcycloalkyl]phenols are consistent with properties identified.

CONCLUSION

1. P-[1(3)-methylcycloalkyl]phenols amino-methylation reactions were carried out. 2-piperidinomethyl-4[1(3)-methylcyclo-alkyl]phenols of 68.8-75.5% yield synthesized as a result of the researches carried out.
2. Chemical structures of the 2-piperidinomethyl-4[1(3)-methylcyclo-alkyl]phenols synthesized by IR, ^{1}H and ^{13}C NMR spectral analyses were confirmed and physicochemical properties determined.

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p-[1(3)-METİLTSİKLOALKİL] FENOLLARIN PİPERİDİNLƏ QARŞILIQLI TƏSİR REAKSİYALARININ BƏZİ XÜSUSİYYƏTLƏRİ

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Məqalədə fenolun 1-metiltsiklopentenlə, 1- və 3- metiltsikloheksenlərlə katalitik tsikloalkilləşmə reaksiyaları nəticəsində alınmış p-[1(3)-metiltsikloalkil] fenolların piperidinlə aminometilləşmə reaksiyaları nəticəsində 2-piperidinometil-4-metiltsikloalkilfenolların sintezindən bəhs edilir. Aminometilləşmə reaksiaları p-tsikloalkilfenolların həlledici iştirakında 30%-li formaldehid və piperidinlə qarşılıqlı təsiri ilə aparılmışdır. Reaksiya 30°C–də 2 saat müddətində həyata keçirilmişdir. Aparılan elmi tədqiqatlar nəticəsində alınmış məqsədli məhsulların çıxımlarının götürülən p-(metiltsikloalkil) fenollara görə 68.8-75.6% təşkil etdiyi müəyyən edilmişdir. 2-Piperidinometil-4-metiltsikloalkilfenolların kimyəvi qurluşları İQ, ^{1}H və ^{13}C NMR spektroskopiya üsulları ilə sübuta yetirilmiş, fiziki-kimyəvi xassələri təyin edilmişdir.

***Açar sözlər**: fenol, 1(3)-metiltsikloalkenlər, tsikloalkilləşmə, p-[1(3)-metiltsikloalkil]fenollar, piperidin, aminometilləşmə, 2-piperidinometil-4-metiltsikloalkilfenollar.*

НЕКОТОРЫЕ ОСОБЕННОСТИ РЕАКЦИЙ ВЗАИМОДЕЙСТВИЯ n-[1(3)-МЕТИЛЦИКЛОАЛКИЛ]ФЕНОЛОВ С ПИПЕРИДИНОМ

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В статье приводится синтез 2-пиперидинометил-4-метилциклоалкилфенолов, полученных в результате аминометилирования п-[1(3)-циклоалкил]фенолов пиперидином, п-[1(3)-циклоалкил]фенолы получают в ходе каталитического циклоалкилирования фенола 1-метилциклопентеном, 1- и 3-метилциклогексенами. Реакции аминометилирования п-циклоалкилфенолов проводили взаимодействием 30%-го формальдегида и пиперидина в присутствии растворителя. Реакция осуществлялась при 30ºС, в течение 2 часов. Было установлено, что выходы полученных целевых продуктов составили 68.8-75.6% по взятому п-(метилциклоалкил)фенолу. Химические структуры 2-пиперидинометил-4-метилциклоалкилфенолов были подтверждены методами ИК, ^{1}H и ^{13}C ЯМР-спектроскопией, определены физико-химические характеристики.

Ключевые слова: *фенол, 1(3)-метилциклоалкены, циклоалкилирование, п- [1(3)-метилциклоалкил]фенолы, пиперидин, аминометилирование, 2-пиперидинометил-4-метилциклоалкилфенолы.*