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CHEMISTRY OF FOSSIL FUEL

Synthesis of Aminomethylated Derivatives of Allylphenols and Study of Their Antimicrobial Characteristics in Motor Oil

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Abstract—A series of nitrogen-containing compounds was synthesized by Mannich condensation of allyl-substituted derivatives of phenol and *o*- and *p*-cresols with formaldehyde and secondary amines. These compounds were studied as antimicrobial additives to motor oil (at a content of 1–2 wt %).

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Nitrogen-containing derivatives of phenols, and in particular Mannich's bases are the subject of systematic studies and, despite numerous papers in this field, still attract researchers' interest, which is caused by their useful functional characteristics [1–5].

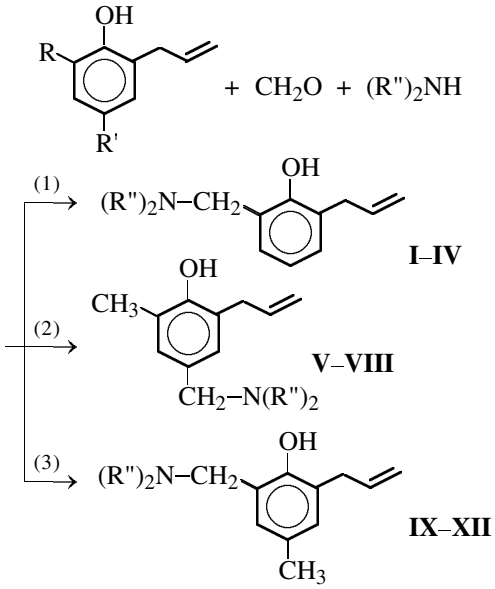
With the aim to synthesize new nitrogen-containing phenols in whole structure an allyl fragment is present, along with aminomethyl group, we examined in this study the reactions of ternary Mannich condensation of 2-allyl-substituted derivatives of phenol and also *o*- and *p*-cresols with formaldehyde and secondary amines.

As can be suggested, the presence of the above substituents in the aromatic core of phenols should impart additional functional properties and, in particular, antimicrobial properties to phenols. Biological protection of oils, fuels, polymers, and other materials is topical problem, since the microbial corrosion of the above materials adversely affects the national economy [6].

EXPERIMENTAL

With the aim to synthesize phenol compounds simultaneously containing an allyl group and amine fragment, we carried out ternary condensation of allyl-substituted derivatives of phenol and *o*- and *p*-cresols with formaldehyde and secondary amines (under the conditions of Mannich's reaction).

Formaldehyde was used in the form of a 37% aqueous solution (Formalin). It was found that the above reaction proceeds well at the equimolar ratio of reactants at 70–75° and duration of 4–5 h to give the corresponding aminomethylated allyl-containing phenols. The target compounds were isolated from the reaction mixture by vacuum distillation. The reaction scheme is as follows:



where (1) at R and R' = H; R" = $-CH_3$ (**I**), $-C_2H_5$ (**II**); $NR"_2$ = –N⟨⟩ (**III**), –N⟨⟩O (**IV**); (2) at R = $-CH_3$; R' = H; R" = $-CH_3$ (**V**), $-C_2H_5$ (**VI**); $NR"_2$ = –N⟨⟩ (**VII**), –N⟨⟩O (**VIII**); (3) at R = H; R' = CH_3; R' = CH_3; R" = $-CH_3$ (**IX**), $-C_2H_5$ (**X**); $NR"_2$ = –N⟨⟩ (**XI**), –N⟨⟩O (**XII**).

The initial allylphenols were synthesized by the well-known procedure [7], Claisen thermal rearrangement of allyl ethers of phenol and *o*- and *p*-cresols, within 3–6 h and were isolated from the reaction mixture by distillation in a high vacuum.

The characteristics of the compounds synthesized are listed in Table 1. Their yield varies from 48.0 to 70.6%, depending on the nature of amine and initial phenol compound. All these compounds, except 4-methyl-2-morpholinomethyl-6-allylphenol (**XII**), are

Table 1. Characteristics of aminomethylated allylphenols

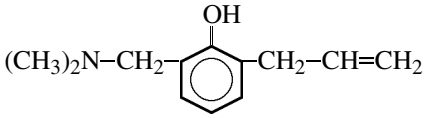
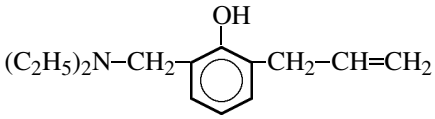
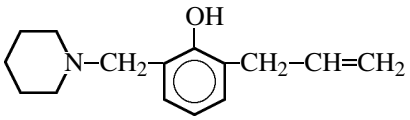
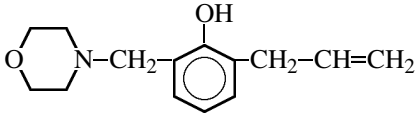
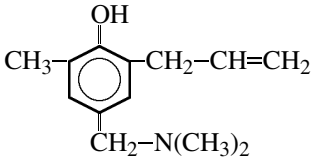
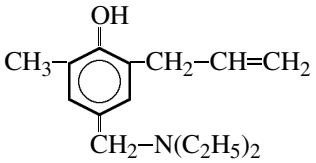
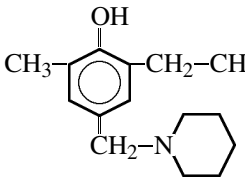
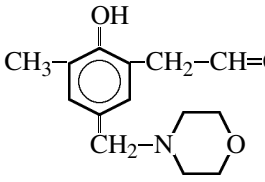
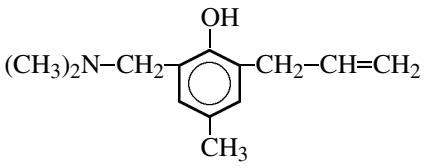
Compound	Yeld, % of theoretical	bp, °C/*P*, mm Hg	n_D^{20}	d_4^{20}, kg m^{-3}
 **I**	48.4	110–111/0.8	1.5298	1015.9
 **II**	70.6	113–114/0.7	1.5285	993.4
 **III**	50.0	118–120/0.8	1.5010	1048.5
 **IV**	70.8	118–119/0.6	1.5030	1091.3
 **V**	45.3	111–113/0.7	1.5012	1023.8
 **VI**	60.0	119–120/0.7	1.5040	1007.9
 **VII**	58.5	124–126/0.6	1.5047	1051.4
 **VIII**	64.0	126–128/0.5	1.5040	1143.5
 **IX**	48.0	110–112/0.6	1.5240	973.2

Table 1. (Contd.)

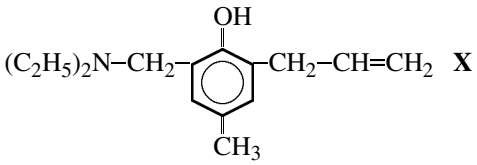
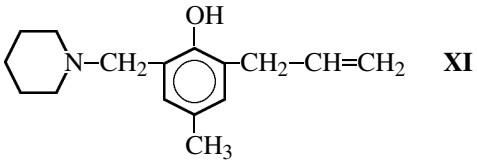
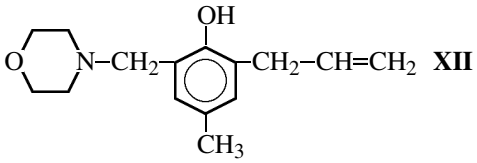
Compound	Yeld, % of theoretical	bp, °C/*P*, mm Hg	n_D^{20}	d_4^{20}, kg m^{-3}
 **X**	63.2	118–120/0.6	1.5210	971.8
 **XI**	52.7	127–129/0.7	1.5064	1033.4
 **XII**	65.2	128–130/0.6	–	–

Table 2. Results of studying antimicrobial characteristics of aminomethylated derivatives of allylphenols in M-12 motor oil

Compound	Concentration in oil, wt %	Area of bacterium annihilation	Area of fungus annihilation
		cm	
2-Dimethylaminomethyl-6-allylphenol (**I**)	1.0	+ +	0.8–1.0
	2.0	+ +	1.6–2.0
2-Diethylaminomethyl-6-allylphenol (**II**)	1.0	+ +	0.9–1.0
	2.0	+ +	1.9–2.0
2-Piperidinomethyl-6-allylphenol (**III**)	1.0	+ +	+ +
	2.0	+ +	1.0–1.2
2-Morpholinomethyl-6-allylphenol (**IV**)	1.0	0.9–1.0	0.7–0.8
	2.0	1.9–2.0	1.5–1.7
2-Allyl-4-dimethylaminomethyl-6-methylphenol (**V**)	1.0	+ +	0.8–1.0
	2.0	+ +	1.7–2.0
6-Methyl-2-allyl-4-diethylaminomethylphanol (**VI**)	1.0	+ +	0.6–0.7
	2.0	1.0–1.1	1.3–1.5
6-Methyl-2-allyl-4-piperidinomethylphenol (**VII**)	1.0	+ +	+ +
	2.0	+ +	1.0–1.1
6-Methyl-2-allyl-4-morpholinomethylphenol (**VIII**)	1.0	+ +	0.7–1.0
	2.0	+ +	1.5–2.1
4-Methyl-2-dimethylaminomethyl-6-allylphenol (**IX**)	1.0	+	+ +
	2.0	+ +	1.0–1.1
4-Methyl-2-diethylaminomethyl-6-allylphenol (**X**)	1.0	+ +	0.7–1.0
	2.0	+ +	1.4–2.0
4-Methyl-2-piperidinomethyl-6-allylphenol (**XI**)	1.0	+ +	0.6–0.9
	2.0	+ +	1.3–1.9
4-Methyl-2-morpholinomethyl-6-allylphenol (**XII**)	1.0	1.1–1.4	0.6–0.9
	2.0	2.2–2.9	1.3–1.9
8-Quinolinol (reference) (**XIII**)	1.0	0.7–1.0	+ +
	2.0	1.5–2.0	+ +
M-12 motor oil (**XIV**) (without additive)	–	+ +	+ +

viscous liquid substances colored from light yellow to brown and readily soluble in aromatic solvents. 4-Methyl-2-morpholinomethyl-6-allylphenol is a light-straw-colored crystalline substance with mp 43°C.

The structures of all the synthesized aminomethylated derivatives of allylphenols were confirmed by the IR and NMR data.

All the compounds were tested as antimicrobial additives to the M-12 motor oil at a content of 1 and 2 wt %. The operations were performed according to GOSTs (State Standards) 9.082–77 and 9.052–88. The nutrient medium for growing the bacterial culture was meat-extract agar (MEA), and for growing the fungus culture, wort agar (WA). The comparison was performed with 8-quinolinol (reference). The results of the tests are presented in Table 2.

As can be seen from Table 2, all the studied aminomethylated derivatives of allylphenols exhibit a fungicidal activity. The diameter of the area of depression of fungus growth, depending on the compound structure and its concentration, is, on the average, 0.8–1.0 (at a content of 1 wt %) and 1.4–2.0 cm (at a content of 2 wt %).

Morpholine-substituted allylphenols also have bactericidial properties and are second in these properties only to 8-quinolinol (reference). As can be seen from Table 2, the latter has no fungicidal activity and the fungus growth was not suppressed in its presence even at a content of 2 wt %. As regards spent M-12 oil, it shows no resistance to fungi and bacteria. The results of comparison tests show that the aminomethylated derivatives of allylphenols are of practical interest and can find application as antimicrobial additives to lubricating oils.

CONCLUSION

Aminomethylated derivatives of allylphenols synthesized by ternary Mannich condensation of allyl-substituted derivatives of phenol and *o*- and *p*-cresols with formaldehyde and secondary amines, when added at a content of 1–2 wt %, have high fungicidal activity with respect to mold fungi. Compounds **IV** and **XII** containing cyclic amine fragment in their structures have also high bactericidal properties (in comparison with the reference, 8-quinolinol).

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