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STUDIES IN THE FIELD OF CHEMISTRY OF NITRO COMPOUNDS (TO 100TH BIRTHDAY ANNIVERSARY OF S. S. NOVIKOV)

Sulfo- and Aminomethylation of 4-Isononylphenol

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Abstract—Possibility of synthesizing sulfo- and aminomethyl derivatives of 4-isononylphenol (**I**) was examined and the anticorrosion activity of the compounds obtained was determined.

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The problem of corrosion control to protect industrial apparatus is rather topical. At present, corrosion inhibitors (CIs) are widely used for protection of equipment from the corrosive effect of the medium. The protective effect of CIs is caused, depending on the chemical nature of their active components, by formation of a hydrophobizing film on the surface of metals or by suppression of electrochemical corrosion processes [1].

It is known that alkylated phenols and their functionally substituted derivatives possess antioxidant and anticorrosive properties and are used as active components of protective additives and corrosion inhibitors [1]. The presence of a nucleophilic hydroxy group and ahydrophobic alkyl substituent in the alkylphenol molecule predetermines their ability to form complexes with atoms and ions of a metal and to hydrophobize its surface.

Of interest as chemical processes improving the anticorrosive properties of alkylphenols are reactions of functional methylation. In particular, high protective properties were found for sulfomethyl and aminomethyl derivatives of alkylphenols.

In order to synthesize active components of corrosion inhibitors, we studied the reactions of sulfo and amino methylation of 4-isononylphenol.

Attempts to sulfomethylate 4-isononylphenol with paraform as a source of formaldehyde and sodium sulfite at an equimolar component ratio in the temperature range 20–95°C failed.

It was found that the sulfomethylation of 4-isononylphenol occurs only in the presence of water. For this reason, the reaction was carried out with formalin (40% aqueous solution of formaldehyde), which supplies in the given case not only formaldehyde, but also the aqueous phase. It was also found that the sulfomethylation of 4-isononylphenol only occurs under the alkaline hydrolysis conditions. The presence of an alkaline medium may be due to partial hydrolysis of sodium sulfite in its dissolution in water:

$$Na_2SO_3 + H_2O \leftrightarrows NaHSO_3 + NaOH.$$

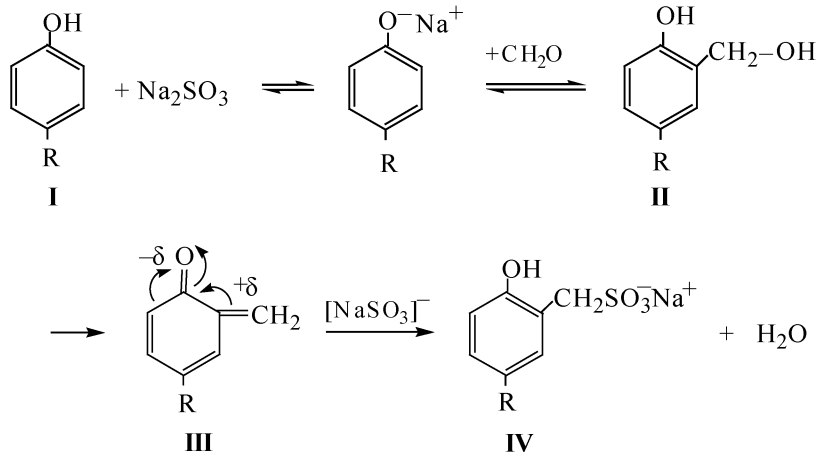
Possibly, the originally formed *ortho*-oxymethyl-4-isononylphenol (**II**) is converted in the alkaline medium to an active electrophilic reagent, 3-methylydene-4-hydroxyisononylbenzyl (**III**). The sodium sulfonate methyl derivative of *para*-isononylphenol (**IV**) is formed via nucleophilic addition of a sodium sulfite anion to **III** (Scheme 1).

Sodium-3-methylene sulfonate-4-isononylphenol (**IV**) was obtained by performing the process in the course of 25 h at a temperature of 90–95°C. The compound exhibits properties of an anion-active surfactant and possesses an anticorrosion activity (84.7%) that compares well with that of the active components of standard formulations.

Aminomethylated derivatives of alkylphenols are cation-active oil-soluble surfactants. The wide use of these compounds as active components of antioxidant additives and corrosion inhibitors is primarily attributed to their ability to form ammonium ions, which interact with negatively charged areas of the metal to give poorly soluble complex compounds of the type of double salts [2].

In this context, we studied the possibility of condensation of **I** with formaldehyde and monoethanolamine. The choice of monoethanolamine as the amine component

Scheme 1.

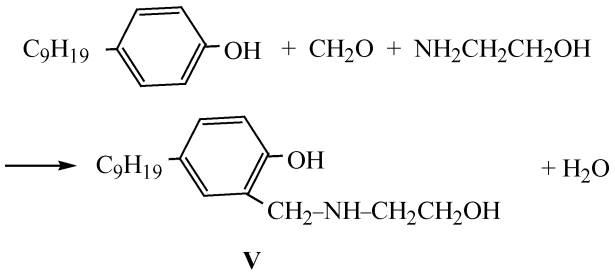


R = *iso*-C_9H_{19}.

is substantiated by its being readily available and by the possibility of introduction of an additional hydroxy group into the liophilic part of the substrate molecule.

The study demonstrated that the condensation of 4-isononylphenol (**I**) with formaldehyde and monoethanolamine yields the expected 2-(hydroxyethyl-aminomethyl)-4-isononylphenol (**V**) only when formaldehyde is used as a paraform by Scheme 2

Scheme 2.

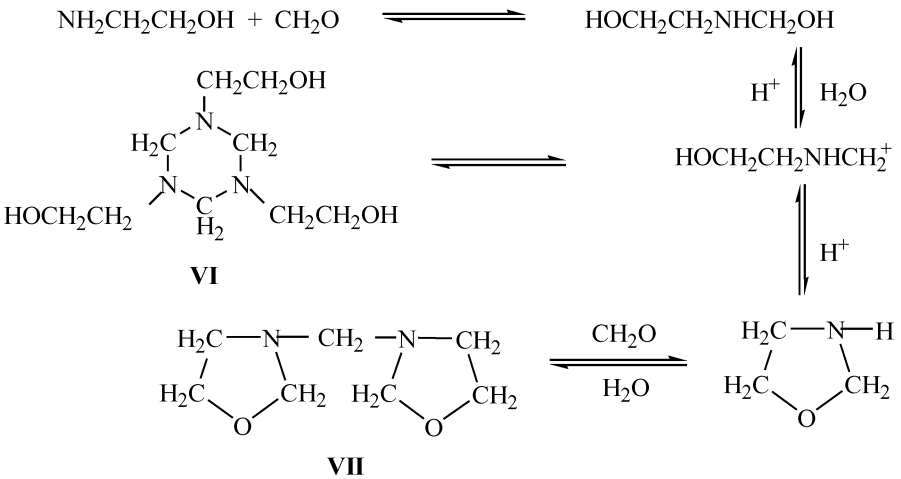


4-Isononylphenol is hardly soluble in water, and, therefore, the reaction does not occur in an aqueous medium, e.g., with the use of formalin. Attempts to activate the process in an aqueous medium by addition of catalytic amounts of acids failed.

It was found that, instead of a mixture of formaldehyde and monoethanolamine, the role of an aminomethylating agent can be played by products of their interaction, which are an equilibrium mixture of 1,3,5-tri(2-hydroxyethyl)-1,3,5-triazacyclohexane (**VI**) *and N,N'*-methylene-bis-oxazalidine (**VII**). The process can be represented by Scheme 3 [3]

It was found that, after removal of water by evaporation in a vacuum at 90°C, compounds **VI** and **VII** react with

Scheme 3.



I to give **V**.

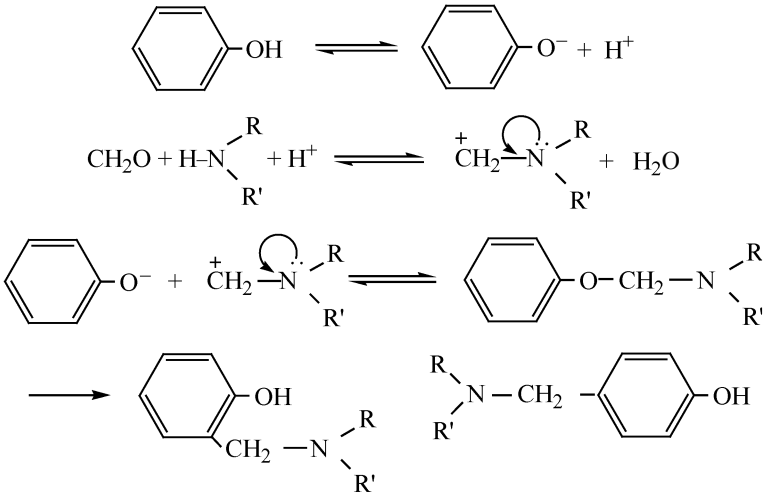
Presumably, the triazine derivative **VI** can be converted under the reaction conditions to *N*'-methylene-bis-oxazalidine (**VII**). The aminomethylation of 4-isononylphenol occurs in the pH range 4–8 at a temperature of 90–95°C. To achieve a high degree of conversion, it is necessary to use an excess amount of aminomethylating agents. Changing the monoethanolamine : formaldehyde ratio from 1 : 1 to 1 : 1.5 does not alter the structure of the final product.

The reaction of amino methylation of phenols is commonly regarded as a particular case of the Mannich reaction. In doing so, it is assumed that the condensation of phenols with amines first yields aminomethyl esters of phenols, which are then regrouped into aminomethyl phenols (Scheme 4).

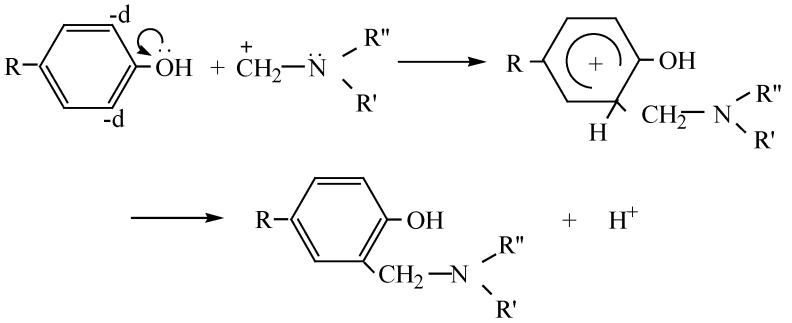
However, formation of aminomethyl esters of phenols could not be confirmed experimentally. Therefore, it seems most likely that the aminomethylation of **I** occurs by the common mechanism of electrophilic substitution at the aromatic ring (Scheme 5).

This statement is confirmed by the fact that not only **I**, but also its polyoxyethylated derivative, Neonol AF-9-6 (**VIII**), undergo aminomethylation (Scheme 6).

Scheme 4.

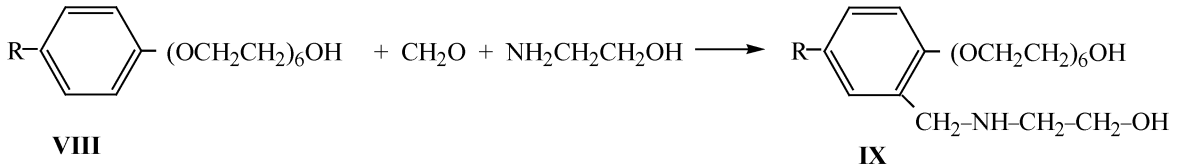


Scheme 5.



R is isononyl (C_9H_{19}); R', H; and R", CH_2CH_2OH.

Scheme 6.



VIII **IX**

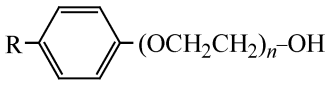
R is isononyl (C_9H_{19}).

Protective effect of corrosion inhibitors at various ratios between the active components, hydroxyethylamino- and sodium methyl sulfonate derivatives of 4-isononylphenol. Total expenditure of the active component 66 mg l–1

Run no	Active component of a corrosion inhibitor, mg l^{-1}		Change in the mass of a plate on its being kept in a corrosive medium, g	Protective effect, %
	sodium sulfonatomethyl derivative of 4-isononylphenol	hydroxyethylaminomethyl derivative of 4-isononylphenol		
1	0	0	0.0883	0
2	0.066	0	0.0308	65
3	0.056	0.010	0.0300	66
4	0.04	0.026	0.0241	73
5	0.033	0.033	0.0178	80
6	0.03	0.036	0.0089	88
7	0.026	0.040	0.077	91
8	0.013	0.053	0.0140	84
9	0	0.066	0.0254	71

The results of the study demonstrated that the reason why the reaction of aminomethylation in direct interaction of **I** with formalin and monoethanolamine is hindered is the thermodynamic phase incompatibility of **I** with aqueous solutions of the reagents. To overcome the barrier of the thermodynamic incompatibility of the reagents, we studied the effect of nonionogenic surfactants on the reaction.

Taking into account the nature of the starting 4-isononylphenol and that of the reagents used in its aminomethylation (monoethanolamine, formalin), we chose, to change the properties of the phase boundary in the reaction system, nonionogenic surfactants: polyoxyethylated alkylphenols (Neonols):



where R is *iso*-C_9H_{19} and n = 6, 12.

The results of the study demonstrated that it is advisable to use Neonol AF-9-6 to accelerate the aminomethylation of **I** with monoethanolamine and formalin.

It was found that, under the reaction conditions at 90°C, Neonol AF-9-6 is rather easily aminomethylated with monoethanolamine and formaldehyde. The reaction is complete in 6–8 h. The aminomethylated Neonol AF-9-6 possesses anticorrosive properties, but is inferior in efficiency to the hydroxyethylaminomethyl derivative **I**. With Neonol AF-9-6 used as an interphase catalyst, the condensation of **I** with formalin and monoethanolamine at 90–95°C is complete in 12–14 h [4].

Taking into account the known facts of appearance of a synergetic effect in joint use of cation- and anion-active surfactants in CIs, we studied how the protective effect depends on the relative amounts of hydroxyethylamino- (**V**) and sodium methyl sulfonate (**IV**) derivatives at their constant total expenditure.

The model formulation is a homogeneous solution containing 33.3% active substrate, nonionogenic surfactants, and a hydrocarbon solvent.

The study was carried out using the gravimetric method [GOST (State Standard) 9.506-2000) on the basis of the loss of mass by a 42 × 22 × 0.2 mm metallic plate of St.3 steel in a standard mineralized solution saturated with hydrogen sulfide (density of 1.2 ± 0.02 g dm^{-3}, hydrogen sulfide content of 1500–2000 g dm^{-3}) at a temperature 20°C in conformity with GOST 9.506–97 at an active component concentration of 66 mg l^{-1}.

The results of the study (see table) demonstrated the advisability of a joint use of hydroxyethylamino- and sodium methyl sulfonate derivatives of 4-isononylphenol in the corrosion inhibitor.

As can be seen from these data, the dependence of the protective properties of the corrosion inhibitor on the ratio between the hydroxyethylamino- and sodium

methyl sulfonate derivatives has an extremal nature with the maximum protective effect (91%) achieved at consumed amounts of the active components of 0.026 and 0.040 mg l^{-1}, respectively. This confirms the occurrence of the synergic effect in joint use of anion- and cation-active surfactants.

CONCLUSIONS

(1) Sulfomethylation of 4-isononylphenol with formaldehyde and sodium sulfite occurs only in an alkaline medium, in the presence of water and a nonionogenic surfactant, via formation of an intermediate, 2-hydroxymethyl-4-isononylphenol. The intermediate is converted in the alkaline medium to 2-methylidene-4-isononyl-3,5-dienecyclohexanone which reacts with the sodium sulfonate anion to give 2-(sodium methyl sulfonate)-4-isononylphenol. The aminomethylation of 4-isononylphenol with formaldehyde and mono- and diethanolamine occurs with an intermediate formation of 3-oxazalidine and its N-hydroxyethyl derivative. The reaction occurs in a weakly acid medium and is accelerated by nonionogenic surfactants.

(2) The sulfo- and aminomethyl derivatives of 4-isononylphenol are, respectively, anion- and cation-active surfactants and exhibit a comparatively high anticorrosion activity in corrosion inhibitors used to protect oil- and gas-producing equipment. Their joint use is promising.

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