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BRIEF COMMUNICATIONS

Substituted *N*-(2-Hydroxyethyl)-1,3-thiazolidin-4-ones: Synthesis and Anticorrosive Properties

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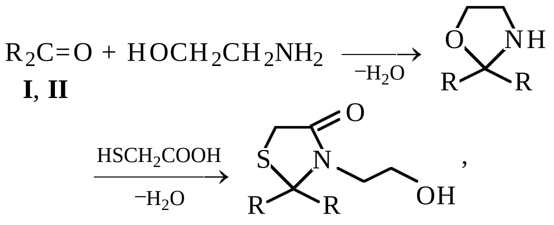
Abstract—A one-pot procedure was developed for synthesis of *N*-(2-hydroxyethyl)-1,3-thiazolidin-4-ones in 64–68% yield by reactions of monoethanolamine with carbonyl compounds and mercaptoacetic acid. The synthesized compounds were characterized by IR and ^{1}H NMR spectra, and their anticorrosive properties were studied.

Nitrogen-containing alcohols and some sulfur-containing organic compounds are known to exhibit anticorrosive properties [1–3]. In this work, we prepared, with the aim to reveal anticorrosive properties of other amino alcohol derivatives, a series of substituted *N*-(2-hydroxyethyl)-1,3-thiazolidin-4-ones and studied them as inhibitors of carbon dioxide and hydrogen sulfide corrosion of steel. One of routes to *N*-(2-hyroxyethyl)-1,3-thiazolidin-4-ones is reaction of oxazolidinies with mercaptoacetic acid [4]. Oxazolidines are, in turn, prepared by condensation of carbonyl compounds with 1,2-amino alcohols [5–7]:



III, **IV**

where R = H (**I**, **III**): R + R = $(CH_2)_5$ (**II**, **IV**).

With this synthesis scheme, the yield of *N*-(2-hydroxyethyl)-1,3-thiazolidin-4-ones **III** and **IV** is 62–63% [4]. The initial oxazolidines were prepared from monoethanolamine and the corresponding carbonyl compounds in 90–94% yield [6, 7].

In this study, we examined the possibility of combining in one-pot synthesis the stages of preparation of oxazolidines and their subsequent transformation into *N*-(2-hydroxyethyl)-1,3-thiazolidin-4-ones.

When developing the synthesis procedure, we took into account the conditions under which the separate stages were performed in [4, 6, 7]. We used benzene as solvent. Condensation of monoethanolamine with carbonyl compounds **I** and **II** was performed by refluxing an equimolar mixture of the reactants, with azeotropic distillation of water. After the release of water was complete, a stoichiometric amount of mercaptoacetic acid was added, and the mixture was refluxed until the release of the next portion of water was complete.

The yield of *N*-(2-hydroxyethyl)-1,3-thiazolidin-4-ones **III** and **IV** under these conditions was 70 and 68%, respectively. The yield of thiazolidinones is the highest at the equimolar ratio of monoethanolamine and carbonyl compounds. With 10% molar excess of the carbonyl compound, the yield decreased by 6–10%, and with 10% molar excess of monoethanolamine, it decreased by 20–25%.

To evaluate the inhibiting power of **III** and **IV**, we studied their effect on steel corrosion under conditions simulating steel corrosion in petroleum production [8].

The anticorrosive activity was evaluated gravimetrically with St. 3 steel samples of size 2 × 20 × 6 mm, according to GOST (State Standard) 9.505–86, in a 1% NaCl solution saturated with CO_2 in the presence of hydrogen sulfide. Tests were performed at 20, 40, and 60°C for 3 h. At a 10^{-3} M concentration of **III** or **IV** and varied temperature, we obtained the following protective effect Z (%): **III**, 95.9 (20°C), 80.5 (40°C), and 45.5 (60°C); **IV**, 96.3 (20°C), 83.3 (40°C), and

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62.7 (60°C). Thus, search for new corrosion inhibitors among thiazolidinone alcohols shows much promise.

EXPERIMENTAL

In syntheses, we used commercial paraform (99.3% purity), cyclohexanone, monoethanolamine, and mercaptoacetic acid, which were purified by distillation to the main substance content of no less than 99.8%.

N-(2-Hydroxyethyl)-1,3-thiazolidin-4-one III. A mixture of 30.5 g (0.5 mol) of monoethanolamine, 15.1 g (0.5 mol) of paraform, and 100 ml of benzene was refluxed with a Dean–Stark trap until the release of water was complete. Then, 46.1 g (0.5 mol) of mercaptoacetic acid was added, and the mixture was refluxed until the release of water was complete. The mixture was cooled and distilled to give 47.9 g (65%) of **II**; bp 176–178°C at 3 mm Hg; mp 63–64°C. IR spectrum (thin film, ν, cm^{-1}): 1630 (C=O), 3300 (OH). ^{1}H NMR spectrum (CDCl$_3$, 90 MHz), δ, ppm: 3.49 t (2H, NCH$_2$), 3.56 d (2H, SCH$_2$CO, ^{4}J 1.4 Hz), 3.76 t (2H, OCH$_2$), 4.0 s (1H, OH), 4.54 d (2H, SCH$_2$N, ^{4}J 1.4 Hz).

Found, (%): C 40.97, H 6.03, N 9.28, S 21.63.
$C_5H_9NO_2S$.
Calculated, (%): C 40.80, H 6.16, N 9.52, S 21.78.

N-(2-Hydroxyethyl)-1-thia-4-azaspiro[4.5]decan-3-one IV was prepared similarly from 30.5 g (0.5 mol) of monoethanolamine, 49.1 g (0.5 mol) of cyclohexanone, and 46.1 g (0.5 mol) of mercaptoacetic acid. Yield 73.5 g (68%); bp 200–203°C at 2 mm Hg; mp 86–87°C. IR spectrum (thin film, ν, cm^{-1}): 1630 (C=O), 3420 (OH). ^{1}H NMR spectrum (CDCl$_3$, 90 MHz), δ, ppm: 1.08–1.79 m [10H, (CH$_2$)$_5$], 3.44 t (2H, NCH$_2$), 3.50 s (2H, SCH$_2$CO), 3.74 t (2H, OCH$_2$), 4.08 s (1H, OH).

Found, (%): C 55.63, H 7.88, N 6.55, S 14.99.
$C_{10}H_{17}NO_2S$.
Calculated, (%): C 55.78, H 7.96, N 6.51, S 14.89.

CONCLUSIONS

(1) Conditions were found for one-pot synthesis of *N*-(2-hydroxyethyl)-1,3-thiazolidin-4-ones from monoethanolamine, carbonyl compounds, and mercaptoacetic acid. The product yield is higher than that in the two-stage synthesis with intermediate isolation of oxazolidines.

(2) The protective effect of *N*-(2-hydroxyethyl)-1,3-thiazolidin-4-ones against carbon dioxide and hydrogen sulfide corrosion of steel reaches 96%.

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