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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

The Reaction of Condensation of Furfural with Mercaptoacetic Acid Esters

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Abstract—The condensation reaction of furfural with various mercaptoacetic acid esters was studied. The reaction products were tested for their corrosion protective properties in M-16 cylinder oil used for marine diesel engines. It was found that the resulting 2-di(alkoxycarbonylmethylthio)methylfuranes at 2% concentration completely suppress corrosion of lead plates.

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Furfural (furan-2-aldehyde) which is produced commercially from pentosan feedstock is known to be the most readily available compound in the furan series [1]. Furfural derivatives are extensively used for preparation of many technically significant products: plasticizers, insecticides, fragrances, medicinal substances, furan resins, etc. [2, 3]. Among furfural derivatives, sulfur- and nitrogen-containing compounds have a prominent place. For example, reactions of furoic acid chlorides with mercaptoaryl- and alkylthiazoles gave sulfur- and nitrogen-containing derivatives of furfural, which were suggested as rubber vulcanization accelerators [2].

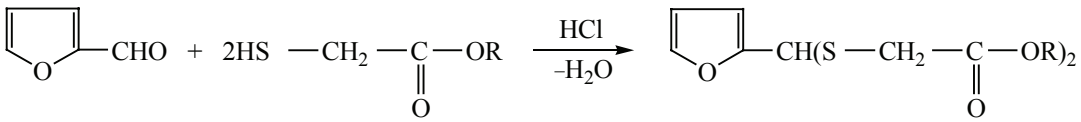
It should be noted that there is continuously growing interest in cyclic compounds containing a furan moiety and various functional groups. Not only conventional preparative but also combinatorial chemistry method are used for synthesis of these compounds [4–6].

Here, we studied the reactions between furfural and various mercaptoacetic acid esters with a view of synthesizing new sulfur-containing furfural derivatives that could be used as lubricant additives.

It was expected that a sulfide sulfur, an ester group, and a furan moiety occurring in these compounds simultaneously would confer to them useful, in particular antioxidant and corrosion protective, functional properties.

EXPERIMENTAL

The new sulfur-containing derivatives of furfural were synthesized by furfural condensation with various alkyl esters of mercaptoacetic acid, catalyzed by small amounts of dilute hydrochloric acid. The condensation reaction scheme was as follows:



where R = *i*-C_3H_7 (**I**), *n*-C_4H_9 (**II**), *n*-C_5H_{11} (**III**), *n*-C_7H_{15} (**IV**), n-C_9H_{19} (**V**).

The reactants, furfural and mercaptoacetic acid, were freshly distilled prior to use; furfural: bp 161.7°C, d_4^{20} 1.159 g cm^{-3}; mercaptoacetic acid: bp 124°C/30 mm Hg, d_4^{20} 1.325 g cm^{-3}.The esters used in this study were obtained by HCl-catalyzed reactions of mercaptoacetic acid with the corresponding aliphatic alcohols, taken in a 1 : 1.2 molar ratio. The reaction was carried out in a three-necked flask equipped with a thermometer, a

stirrer, and a reflux condenser. The calculated amounts of mercaptoacetic acid and aliphatic alcohol and a few drops of concentrated hydrochloric acid were charged into the flask under stirring, and the resulting mixture was refluxed for 10 h. Upon completion of the reaction the resulting mass was diluted with benzene (1 : 3), transferred to a separation funnel, and washed several times with water. The organic layer was separated, dried over sodium sulfate, and subjected to distillation. Table 1 summarizes the characteristics of the mercaptoacetic acid esters synthesized.Mercaptoacetic acid esters are colorless liquids, highly soluble in organic solvents. Their structure was confirmed by IR spectroscopy.The condensation reaction of furfural with the mercaptoacetic acid esters synthesized was also carried out in a three-necked flask equipped with a thermometer, a stirrer, a dropping funnel, and a reflux condenser. The calculated amounts of furfural and catalyst, dilute hydrochloric acid, were charged into the flask, and the resulting mixture was stirred and then thoroughly cooled (to 0–6°C). Next, the calculated amount of mercaptoacetic acid ester was fed from the dropping funnel at this temperature for 1 h, after which the mixture was further stirred at 15–6°C for 2 h.

Upon completion of the reaction the condensate was 1 : 2 (w/w) diluted with benzene, transferred to a separation funnel, and washed several times with water. The organic layer was separated, dried over sodium sulfate, and subjected to vacuum distillation.

We examined the yields of the target compounds **I–V** as influenced by various factors (reactant ratio, nature of mercaptoacetic acid ester, temperature, reaction time) and determined the best conditions for their synthesis: temperature from 0 to –5°C, catalyst (HCl) amount 2% (for the mixture taken), and furfural:ester molar ratio 1 : 2.

Table 2 lists the characteristics of the target products synthesized, 2-di(alkoxycarbonylmethylthio)methylfuranes **I–V**.

The structure of the sulfur-containing furfural derivatives synthesized was confirmed by NMR spectroscopy, with compounds I and II as examples. The NMR spectra were recorded on a Bruker-300 (Bruker, FRG) instrument with tetramethylsilane as internal standard.

Compound I. ^{1}H NMR spectrum (CCl_4), δ, ppm: 25 d (12H, $4CH_3$, $^3J_{H–H}$ = 6.28 Hz), 3.15 and 3.35 d (4H, $2SCH_2$), 4.98 m (2H, OCH), 5.41 s (1H, SCH), 6.3 and 6.31 d (2H, 2CH=, $^3J_{H–H}$ = 3.25 Hz), 7.45 s (1H, =CHO). ^{13}C NMR spectrum (CCl_4), δ, ppm: 22, 33, 47, 69, 108, 110, 149, 150, 168.

Compound II. ^{1}H NMR spectrum (CCl_4), δ, ppm: 0.9 t (6H, $2CH_3$, $^3J_{H–H}$ = 6.38 Hz), 1.35 m (4H, $2CH_2$), 1.6 m (4H, $2CH_2$), 3.15 and 3.42 d (4H, $2SCH_2$), 4.05 t (4H, $2OCH_2$), 5.45 (1H, SCH), 6.3 d (2H, 2CH=, $^3J_{H–H}$ = 3.27 Hz), 7.35 s (1H, =CHO). ^{13}C NMR spectrum (CCl_4), δ, ppm: 14, 19, 30, 33, 38, 46, 65, 108, 110, 149, 150, 168.

To test the suitability of the compounds synthesized as

Table 1. Characteristics of mercaptoacetic acid esters

R	bp, °C/P, mm Hg	Yield, %	n_D^{20}	d_4^{20}, g cm^{-3}
i-C_3H_7	165–166	57.0	1.4509	1.0408
n-C_4H_9	193–194	54.3	1.4568	1.0268
n-C_5H_{11}	202–204	59.6	1.4574	1.0276
n-C_7H_{15}	105–107/1	56.0	1.4590	1.0115
n-C_9H_{19}	118–119/ 1	60.0	1.4609	0.9532

Table 2. Characteristics of target compounds

Compound	bp, °C/2 mm Hg	Yield, %	n_D^{20}	d_4^{20}, g cm^{-3}
I	83–85	70.0	1.5180	1.1814
II	90–93	64.7	1.5120	1.1433
III	117–120	62.0	1.5090	1.1326
IV	127–129	60.5	1.5074	1.1070
V	135–137	60.0	1.5012	1.0117

Table 3. Results of testing compounds **I–V** in M-16 cylinder oil

Compound	Concentration in oil, %	Corrosivity toward lead, g m^{-2}
I	1	3.5
	2	0
II	1	10.7
	2	3.3
III	1	11.6
	2	2.7
IV	1	12.0
	2	1.3
V	1	12.4
	2	2.1
Neat oil (no additive)	–	256

corrosion protective additives in oils, we prepared their compositions with M-16 cylinder oil used in marine diesel engines and carried out tests with lead plates on a DK-NAMI instrument at 140°C. The results are summarized in Table 3.Studies of the furfural condensation reaction with various mercaptoacetic acid esters showed that, depending on the length of the radical R in the ester group, the target 2-di(alkoxycarbonylmethylthio)methylfuranes were obtained in a 60 to 70% yield, i.e., with increasing length of the radical R the yield tends to decrease, as expected (Table 2). The n_D^{20} and d_4^{20} characteristics exhibit similar trends. The compounds synthesized are viscous yellow substances, highly soluble in lubricating oils. Table 3 shows that all the sulfur-containing compounds synthesized possess high corrosion protective properties with respect to lead plates. At 1% concentration of these compounds in M-16 oil the corrosivity was estimated at 3.5–12.4 g m^{-2}, and at 2% concentration corrosion was virtually completely suppressed. As for neat M-16 cylinder oil (without additives), it does not possess the required protective properties: Its corrosivity toward lead is 256 g m^{-2}.

Thus, our tests showed that the sulfur-containing compounds synthesized by condensation of furfural with mercaptoacetic acid esters are suitable as corrosion protective additives for M-16 cylinder oil used in marine diesel engines.

CONCLUSIONS

(1) Hydrochloric acid-catalyzed condensation reactions of furfural with various mercaptoacetic acid esters were studied.

(2) The 2-di(alkoxycarbonylmethylthio)methylfuranes synthesized were tested at 1 and 2% concentrations as corrosion protective additives to M-16 cylinder oil used in marine diesel engines. It was found that they possess high corrosion protective properties and virtually completely suppress corrosion of lead plates.

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