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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis of New Polyfunctional Additives to Lubricating Oils

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Abstract—Possibility of synthesizing new polyfunctional sulfur-, phosphorus-, and zinc-containing compounds with anti-wear and anti-scuff properties, promising as high-efficiency additives to lubricating oils, was studied.

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Alkyl, cycloalkyl, and aryl dithiophospates of metals (Zn, Mo, Ba, Cu, Ca) are widely used as additives improving the lubricating, antioxidant, and anticorrosive properties of mineral oils [1–4]. Heteroatomic compounds containing nitrogen, boron, phosphorus, and sulfur atoms are introduced into these additives to improve their efficiency [5]. The effect of heteroatomic additives is based on that a metal-organic film is formed and prevents direct contact between friction surfaces. In addition, owing to the low, compared with steel, melting point of iron sulfide in the case of sulfur-containing additives, the sulfide film precludes scuffing and seizure of contacting surfaces [6–8].

In order to extend the range of highly efficient and competitive polyfunctional additives to transmission oils, which would be promising for practical use and simultaneously exhibit anti-wear and anti-scuff properties, new types of additives were synthesized from zinc dithiophosphates containing trithiolane substituents produced from readily accessible methylol norbornene and aliphatic and cyclic alcohols as raw materials.

EXPERIMENTAL

The compounds synthesized were analyzed by the GLC method on Khrom-5 and Khrom-41 instruments, with a flame-ionization detector, 1.2 m × 3 mm and 2.4 m × 3 mm columns packed with 5% SE on N-AW Chromaton, and helium as carrier-gas (50 ml min^{-1}). 1H NMR spectra were recorded on an Tesla BS-467 instrument (60 MHz) relative to TMS in CDCl3, and 13C NMR spectra, on a Jeol-FX-90Q spectrometer with broadband proton suppression in the homoresonance mode with partial retention of the nuclear Overhauser effect, in $CDCl_3$ relative to TMS. Mass spectra were obtained on an MX-1306 instrument with an ionizing electron energy of 70 eV and ionization chamber temperature of 200°C.

The anti-wear and anti-scuff properties of the zinc dithiophosphates synthesized were tested on a four-ball friction machine with ShKh-15 steel balls 12.7 mm in diameter at a relative sliding velocity of friction surfaces of 0.54 m s^{-1} and rotation rate of 1420 rpm. The zinc dithiophosphates were introduced into TS-14.5 oil in an amount providing that the sulfur content was about 0.8 wt %, The mean Hertz load (MHL), critical load P_{cr}, and welding load P_w were determined with a step-by-step increase in the load.

A thermostated glass reactor equipped with an efficient stirrer, thermometer, and reflux condenser was charged with 50 mmol of 2-methylolbicyclo[2.2.1]hept-5-ene (1) (4 : 1 mixture of stereoisomers of endo and exo configurations) and 1 mol % catalyst. The temperature was raised to 125°C and 150 mmol of elementary sulfur was added under vigorous agitation in the course of 30 min. The reaction mass was agitated for 6 h and then cooled. The reaction products were extracted with petroleum ether (bp 42–64°C), which was then removed in a vacuum at room temperature. Column chromatography was used to isolate 8-methylol-3,4,5-trithiatricyclo[5.2.1.02,6[decane (2) from the residue as a mixture of endo-and exo-isomers in total yield of 75%; bp 54.5–55°C. 1H NMR spectrum, δ, ppm: 1.29–2.00 (m, 5H, CH_2), 2.17–2.48 (m, 2H, CH), 3.32–3.75 (m, 2H, CHS), 3.93–4.00, 4.24 + –4.31 (m, 5H, CH_2O).

Found (%): C 40.08, H 5.00, O 13.02, S 41.2

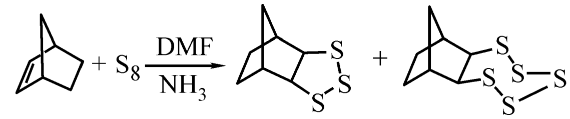
Calculated (%): C 40.68, H 5.08, O 13.56, S 40.68

endo-8-Methylol-*endo*-3,4,5-trithiatricyclo[5.2.1.02,6] decane (2a) ^{13}C NMR spectrum, δ, ppm: 41.08 d (C1), 68.98 d (C2), 63.84 d (C6), 42.64 d (C7), 40.69 d (C8), 33.34 t (C9), 30.74 t (C10), 61.43 t (C11).

8-Methylol-*exo*-3,4,5-trithiatricyclo[5.2.1.02,6]decane (2) ^{13}C NMR spectrum, δ, ppm: 43.81 d (C1), 70.08 d (C2), 69.82 d (C6), 46.22 d (C7), 40.49 d (C8), 36.33 t (C9), 28.98 t (C10), 61.69 t (C11).

A 20-mmol portion of 8-methylol-3,4,5-trithiatric yclo[5.2.1.02,6]decane (2) obtained under the optimal conditions was mixed with an equimolar amount of a solution of the corresponding alcohol in toluene. Then 10 mmol of phosphorus pentasulfide (P_2S_5) was added and the mixture was kept under agitation at a temperature of 90°C for 5 h. As a result, partial dithiophosphoric acid esters (3a–3d) were obtained in 95% yield. The reaction of 10 mmol of esters (3a–3d) with 5 mmol of ZnO (65°C, 5 h) gives in nearly quantitative yield the corresponding zinc dithiophosphates (4a–4d) containing a tricyclic substituent with trithiol sulfur.

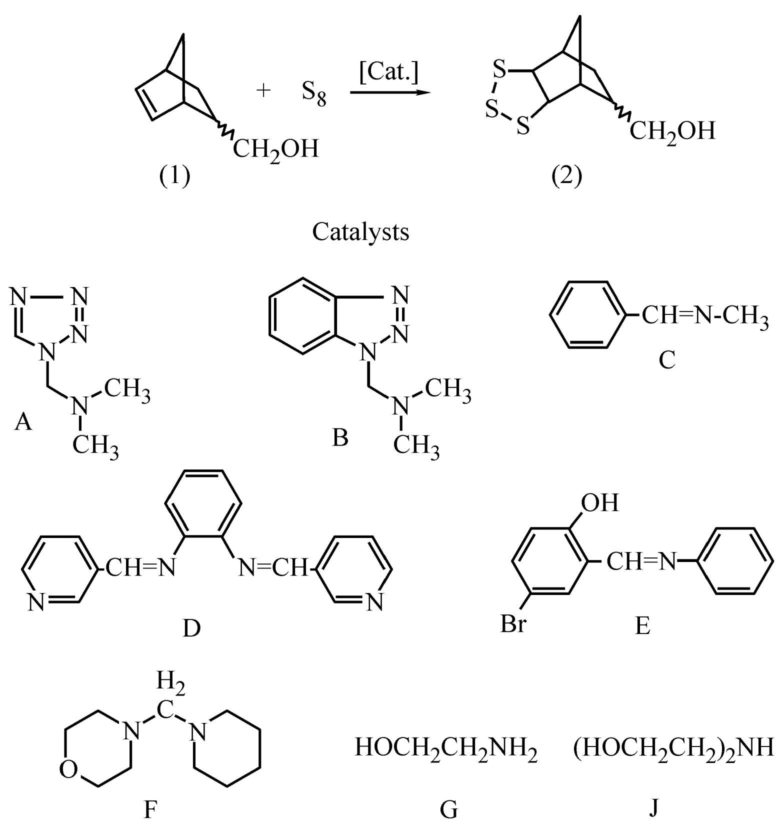
It is known that the reaction of norbornene (or norbornadiene) with elementary sulfur in DMFA saturated with NH_3 gives the corresponding tri- and pentathiolanes at the norbornene double bond in a rather high yield [9, 10]:



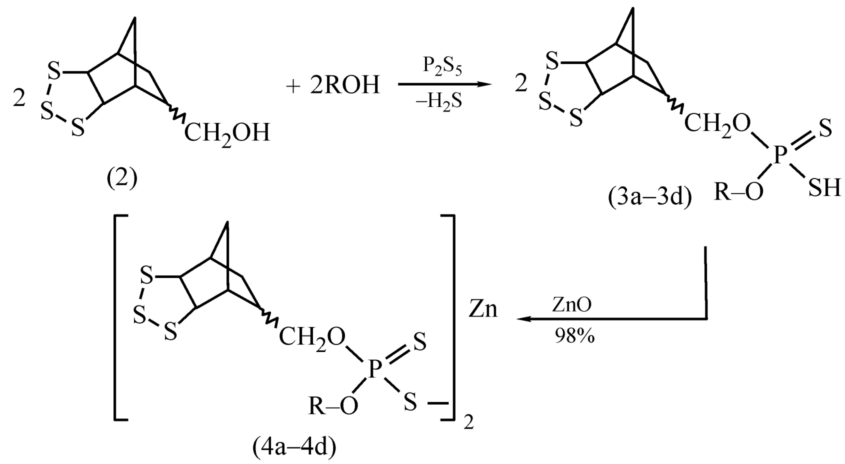
To obtain compounds of this kind (trithiolanes), which contain a primary hydroxy group that can enter into the reaction with P2S5 to give dithiophosphoric acid esters, the reaction of 2-methylolbicyclo[2,2,1]hept-5-ene with sulfur (S8) was studied under the conditions reported in [9, 10]. It was found that this reaction occurs with the highest selectivity in the target trithiolane (2) and high yield when methylol norbornene is thiylated with S8 in the presence of amines with various structures.

For example, the reaction of 2-methylobicyclo[2.2.1]-hept-5-ene (1) [4 : 1 mixture of *endo* (1a) and *exo* (1b) stereoisomers] with a threefold excess of cyclooctasulfane (S8) in the presence of catalytic amounts of primary,

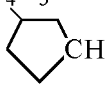
Scheme 1.



Scheme 2.



(a) R = n-$C_3H_7CH_2$, (b) R = $CH_3(CH_2)_3CH(C_2H_5)CH_2$, (c) R = $CH_3CHCH_2CH_2$ C_2H_5 CH_3 and (d) R = n-C_4H_5



secondary, or tertiary amines , and also Schiff bases or substituted triazoles, at 125°C gives in 6 h *endo/exo*-8-methylol-3,4,5-trithiatricyclo[5.2.1.02,6]decane (2) in 65–90% yields (Scheme 1).

Among the amines tested in this reaction, the highest catalytic activity is observed for 1-(*N,N*-dimethyl-aminomethyl)-1,24-triazole (A) (Table 1). The yield in the chosen conditions [(1) : S8 : catalyst molar ratio 1 : 3 : 0.02] reaches a value of 90%.

Table 1. Effect of catalyst nature and reaction conditions on the yield of 8-methylol-3,4,5-trithiatricyclo[5.2.1.02,6]-decane (2)

Catalyst, mol %	τ, h	*T*, °C	Yield of (2), %
–	6	125	20
[A]:			
0.5	6	125	55
1	6	125	75
2	6	125	90
1	4	125	60
1	6	130	80
[B], 1	6	125	70
[C], 1	6	125	55
[D], 1	6	125	65
[E], 1	6	125	60
[F], 1	6	125	55
[G], 1	6	125	65
[J], 1	6	125	60

8-Methylol-3,4,5-trithiatricyclo[5.2.1.02,6]decane (2) was studied in the reaction with phosphorus pentasulfide and n-butanol [90°C, (2): n-butanol : P_2S_5 molar ratio 2 : 2 : 1.1] (Scheme 2).

To find out how the structure of an alcohol affects properties of zinc dithiophosphates (4a–4d), 2-ethylhexanol, 5-ethyloctan-2-ol, and 3-(n-butyl)cyclopentanol were introduced into the reaction with phosphorus pentasulfide, together with n-butanol.

The reaction of partial dithiophosphoric acid ester (3a) with ZnO gives, in nearly quantitative yield, zinc dithiophosphate containing a tricyclic substituent with trithiol sulfur.

The results of tests with the compounds synthesized demonstrated that partial dithiophosphoric acid esters (3a–3d) and zinc dithiophosphates (4a–4d) possess better anti-wear and anti-scuff properties than the known DF-11 additive (5) (Table 2) and can be used as high-efficiency additives to lubricating oils.

As can be seen from the results presented, compounds (4a) and (4b) are the most promising additives.

CONCLUSIONS

High-efficiency sulfur-, phosphorus-, and zinc-containing anti-wear and anti-scuff additive for manufacture of high-quality lubricating oils can be synthesized from methylol norbornene trithiolane.

Table 2. Results of tests of the polyfunctional additives synthesized

Compound	Formula	MHL	P_{cr}	P_{cw}	Found, % / Calculated, %			
			kg		Zn	S	C	H
(2)	$C_7H_9S_3CH_2OH$	57.0	100	266	–	42.98/43.64	43.15/43.64	5.62/5.45
(3a)	$(C_8H_{11}S_30)(C_4H_90)\underset{\underset{S}{\Vert}}{P}SH$	72.7	100	355	–	40.67/41.24	36.72/37.11	5.35/5.45
(3b)	$(C_8H_{11}S_30)(C_8H_{17}0)\underset{\underset{S}{\Vert}}{P}SH$	57.0	100	335	–	36.65/36.04	42.62/43.24	6.27/6.53
(3c)	$(C_8H_nS_30)(C_{10}H_{21}0)\underset{\underset{S}{\Vert}}{P}SH$	57.0	100	335	–	33.12/33.90	46.33/45.78	6.58/6.99
(3d)	$(C_8H_nS_30)(C_9H_{17}0)\underset{\underset{S}{\Vert}}{P}SH$	57.0	100	335	–	34.47/35.08	45.18/44.74	6.14/6.36
(4a)	$[(C_8H_{11}S_30)(C_4H_90)\underset{\underset{S}{\Vert}}{P}S]_2Zn$	75.4	112	447	7.11/7.75	38.97/38.14	33.52/34.33	4.29/4.77
(4b)	$[(C_8H_{11}S_30)(C_8H_{17}0)\underset{\underset{S}{\Vert}}{P}S]_2Zn$	70.2	112	422	7.49/6.83	33.08/33.65	39.84/40.38	5.43/5.89
(4c)	$[(C_8H_{11}S_30)(C_{10}H_{21}0)\underset{\underset{S}{\Vert}}{P}S]_2Zn$	70.2	100	398	6.73/6.45	31.29/31.78	42.18/42.90	6.17/6.36
(4d)	$[(C_8H_{11}S_30)(C_{11}H_{21}0)\underset{\underset{S}{\Vert}}{P}S]_2Zn$	70.2	100	398	6.58/6.30	31.69/31.04	43.41/44.23	6.07/6.21
(5)	$[(C_4H_90)(C_8H_{17}0)\underset{\underset{S}{\Vert}}{P}S]_2Zn$	56.0	100	251	10.54/10.93	21.04/21.39	49.0/48.29	8.22/8.69

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