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# Synthesis and antioxidant properties of novel 1,2,4-triazoles with 2,6-di-tert-butylphenol fragments

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**Abstract.** This work describes the synthesis of novel derivatives of 1,2,4-triazole containing a hindered phenol fragment. Influence of the obtained compounds on the thermal-oxidative stability of the sealing liquid AG-4I was investigated. Triazolothiazoles with long alkyl substituents were found to exhibit better antioxidant properties compared to Agidol-1.

## 1. Introduction

Antioxidants are of great interest for the oil and gas industry as additives to motor fuels, lubricants, plasticizers, improving their antioxidant stability required during operation, as well as during storage and transportation.

Antioxidant additives are used to improve the thermal-oxidation properties and slow down the oxidation of the lubricating oil, thus preventing the formation of corrosive products. Various types of antioxidants differing in their mechanism of action have been described:

- Inhibitors of free radical reactions (radical scavengers), their mechanism of action is to transfer a free radical from an active peroxide molecule to an antioxidant molecule with the formation of an inactive, highly screened radical [1];
- Antioxidants that decompose hydroperoxides, capable to react with hydroperoxides and to break them down into molecular products, without the formation of free radicals [2];
- Metal passivators, blocking the catalytic activity of metals contained in oils (metals such as zinc, copper, molybdenum are often included in additives, and iron also enters the oil due to surface wear) due to the formation of a film on the metal surface or through the formation of chelating complexes (chelating agents) [3].

At the present time, there is a steady interest of researchers in new antioxidants containing in their structure a heterocyclic fragment. One of the most common antioxidants that decompose peroxides are dialkylmercapto-1,3,4-thiadiazoles [4]. Antioxidants-passivating metals are derivatives of quinizarin, benzotriazole, benzimidazole and indole [5]. In a number of works it has been shown that derivatives of imidazole, triazole, imidazoline, thiazole, thiazine [6-7] also exhibit antioxidant activity in mineral oils.

One of the promising approaches to the creation of new antioxidants is the combination of fragments acting by different mechanisms in their molecule. Thus, new derivatives of benzothiazole [8], benzotriazole, dihydropyrano[2-3], pyrazole [9], thiadiazole [10], containing phenol as a substitute, were found to exhibit antioxidant properties.



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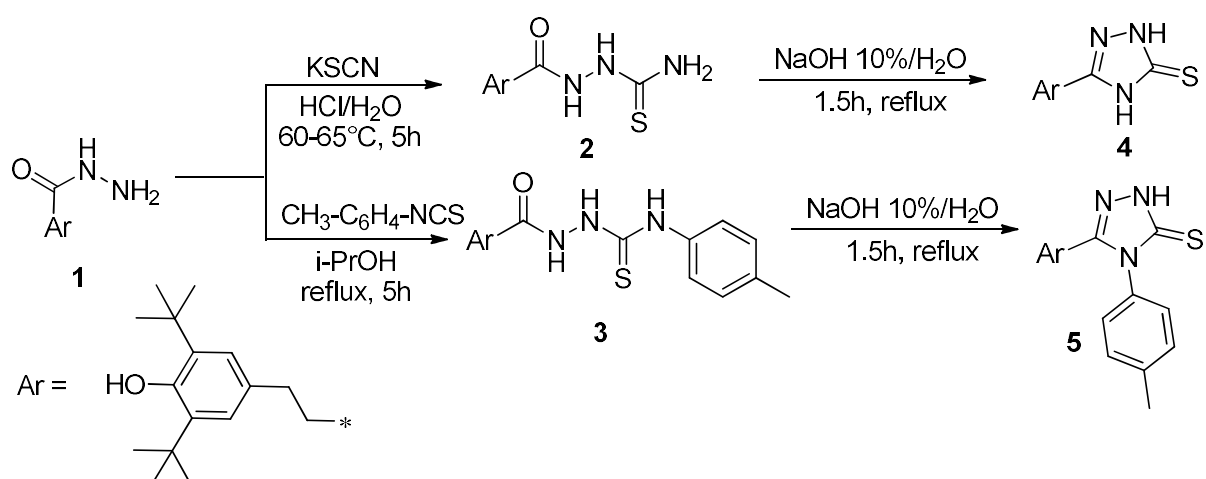
In continuation of studies of the antioxidant ability of heterocycles with phenolic fragments [11], in this work some derivatives of 1,2,4-triazole were obtained and their effect on the thermooxidative stability of sealing liquid was investigated.

## 2. Materials and methods

The NMR  $^1\text{H}$  and  $^{13}\text{C}$  spectra of solutions in  $\text{DMSO-d}_6$  and  $\text{CDCl}_3$  were recorded on a Bruker AM-300 spectrometer (Karlsruhe, Germany). All experiments were performed according to the standard methods of Bruker. Chemical shifts were reported relative to  $\text{Me}_4\text{Si}$ . The values of SSCCs are given in Hz. The mass spectra were recorded on an MS-30 Kratos device (Eu, 70 eV). A peak of the molecular ion  $\text{M}^+$  was observed for all synthesized compounds. The melting points of the compounds obtained were determined in an open capillary. Elemental analysis was carried out using Elemental analyzer Vario micro cube (Langensfeld, Germany). The course of reactions and purity of the compounds obtained was monitored by TLC on silica gel plates in a 10:1 chloroform-ethanol solvent system.

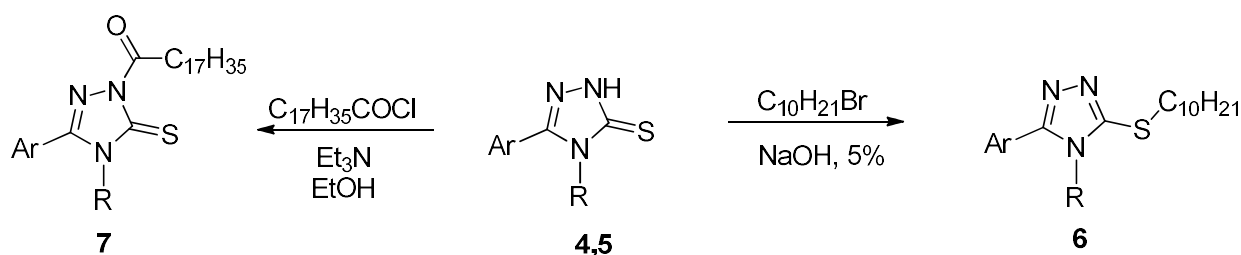
## 3. Results

The triazoles were obtained according to the schemes shown in figures 1-3. Initially, the reaction of 3-(4-hydroxy-3,5-di-tert-butylphenyl) propanoic acid hydrazide **1** with potassium thiocyanate gave 1-acylthiosemicarbazide **2**. During the reaction of the starting hydrazide with *p*-tolliothiocyanate, 1-acylthiosemicarbazide **3** was synthesized. Cyclization of **2** and **3** in sodium hydroxide solution led to the formation of 1,2,4-triazole-5-thiones **4** and **5**.



**Figure 1.** The scheme of preparation of 1,2,4-triazole-5-thiones.

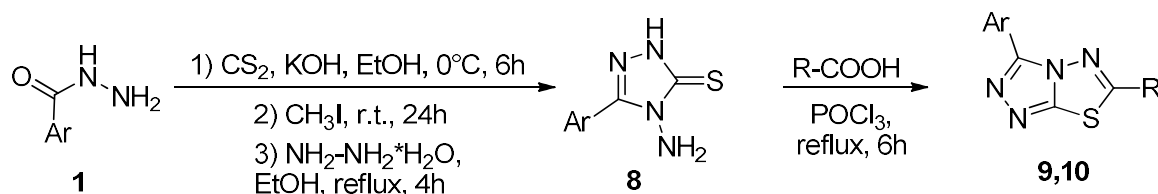
To increase the solubility of triazoles in hydrocarbon media, long alkyl chains were introduced into their structure. Triazole **4** was alkylated with decylbromide, triazole **5** was acylated with stearic acid chloride.



$\text{Ar} = 4\text{-HO-3,5-(t-Bu)}_2\text{-C}_6\text{H}_2\text{-}$      $\text{R} = \mathbf{4,6}$ : H;  $\mathbf{5,7}$ :  $4\text{-CH}_3\text{-C}_6\text{H}_4\text{-}$

**Figure 2.** The scheme the reaction between 1,2,4-triazole-5-thiones and electrophilic reagents.

To obtain condensed rings with a hindered phenol fragment based on hyrazide **1**, the dithiocarbazine acid methyl ester was obtained, and upon refluxing with hydrazine hydrate, cyclized to 4-amino-1,2,4-triazole-5-thione **8**. During the reaction of **8** with stearic acid and with palmitic acids in POCl<sub>3</sub>, thiaolotriazoles **9** and **10** were obtained.



Ar = 4-HO-3,5-(t-Bu)<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>- R = **9**: C<sub>17</sub>H<sub>35</sub>; **10**: C<sub>15</sub>H<sub>31</sub>

**Figure 3.** The scheme of preparation of triazolothiazoles.

In all cases, after the completion of the reaction, the reaction mixture was poured into water, the precipitate that formed was filtered off and recrystallized from a suitable solvent. The structure of the obtained compounds was proved by IR and NMR spectroscopy, mass spectrometry, and elemental analysis.

#### 4. Discussion

The yields, melting points, solvents for recrystallization and spectral data of the obtained compounds are presented in table 1. All compounds were obtained in good yields of 43-77%. NMR spectral data are consistent with the structures.

The antioxidant properties of the obtained substances were investigated in the sealing fluid AG-4I, the concentration of the additives was 0.5%. Oxidation was carried out on a Papok-R device at 140°C for 6 h.

The efficiency of antioxidant additives was assessed by the relative change in the dynamic viscosity before and after oxidation of the AG-4I sealing liquid with the corresponding additives, as well as by the optical density of the 1700 cm<sup>-1</sup> band in the IR spectra. The Agidol-1 additive was used as a reference, its efficiency was found to be 24.21%.

All compounds except triazole **6** exhibited antioxidant efficiency. The best results were shown by triazolothiazole **9**, in the presence of which the relative change in dynamic viscosity was 12.6%, but at the same time, the content of oxidation products in the sample with **9** after the test is slightly higher than that in the reference sample. The sample with triazolothiazole **10** which contain shorter alkyl chain in comparison with **9** showed higher changes in dynamic viscosity, but lower content of oxidation products according to IR spectra. Substance **4** caused an increase in oxidation products content, but the viscosity decreased in much the same way as in the reference sample. An interesting effect was observed for compound **7**, in the presence of which the content of oxidation products was close to zero, but the dynamic viscosity after oxidation increased by 4.31%, this fact requires further study.

#### 5. Conclusion

In this work, number of previously undescribed derivatives of 1,2,4-triazole was synthesized. The structure of the obtained compounds was proved by IR, <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy, mass spectrometry, and elemental analysis. The study of the antioxidant activity of the synthesized compounds showed that triazolethiazoles **9** and **10**, containing a hindered phenol fragment and a long alkyl substituent (C<sub>17</sub>, C<sub>15</sub>), are promising antioxidants for sealing liquids.

**Table 1.** Physical and spectral data of the compounds obtained.

No	Yeld, %	Melting point, °C	Spectral data
2	75	157-159 CHCl <sub>3</sub>	IR spectrum (v, cm <sup>-1</sup> ) 1688 (C = O), 3178, 3261 st (-NH-NH <sub>2</sub> ). <sup>1</sup> H NMR δ (ppm): 1.35 s (18H, t-Bu), 2.42 t (2H, CH <sub>2</sub> ), 2.71 t (2H, CH <sub>2</sub> ), 6.72 s (1H, HO), 6.89 s (2H, Har), 9.43 w. s. (2H, NH), 10.25 s (1H, NH). MS: (M +), m/z 351. Calc.,%: C 61.51; H 8.32; N 11.95; S 9.12; found,%: C 61.41; H 8.43; N 12.02; S 9.26.
3	77	203-204 i-PrOH: water 1: 1	<sup>1</sup> H NMR δ (ppm): 1.35 s (18H, t-Bu), 2.31 s (3H, CH <sub>3</sub> ), 2.44 t (J = 7.3, 2H, CH <sub>2</sub> ), 2.75 t (J = 7.2, 2H, CH <sub>2</sub> ), 6.71 s (1H, OH), 6.97 s (2H, Har), 7.14 d (2H, Har), 7.30 d (2H, Har), 9.48 w.s. (2H, NH), 9.86 s (1H, NH). MS: (M +) m / z 444. Calc.,%: C 67.99; H 7.99; N 9.51; S 7.26; found,%: C 67.81; H 7.85; N 9.68; S 7.36;
4	80	214-217 °C EtOH: water 1: 1	<sup>1</sup> H NMR δ (ppm): 1.4 s (18H, t-Bu), 2.44 t (2H, CH <sub>2</sub> ), 2.65 t (2H, CH <sub>2</sub> ), 6.70 s (1H, HO), 6.95 s (2H, Har), 13.11 s (1H, NH) Calc.,%: C, 64.83; H, 8.16; N, 12.60; S, 9.61; found,%: C, 64.95; H, 8.07; N, 12.72; S, 6.68.
5	76	190-191 °C i-PrOH: water 1: 1	<sup>1</sup> H NMR δ (ppm): 1.35 s (18H, t-Bu), 2.38 t (2H, CH <sub>2</sub> ), 2.65 t (2H, CH <sub>2</sub> ), 2.34 s (3H, CH <sub>3</sub> ), 6.62 s (1H, OH), 6.71 s (2H, Har), 7.08 d (2H, Har), 7.32 d (2H, Har), 13.60 s (1H, NH). Calc.,%: C, 70.88; H, 7.85; N, 9.92; S, 7.57; found,%: C, 70.95; H, 7.83; N, 9.78; S, 7.75.
6	65	153-155°C benzene: hexane 1: 1	<sup>1</sup> H NMR δ (ppm): 0.85 t (J = 7.1), 1.26 s, 1.35 s (18H, t-Bu), 2.18 t (J = 7.3, 2H, CH <sub>2</sub> ), 2.34 s (2H, CH <sub>2</sub> ), 2.67 s (2H, CH <sub>2</sub> ), 6.68 s (1H, OH), 6.73 s (2H, Har), 11.73 s (NH, 1H), 13.24 s (1H, NH). MS: (M +) m/z 473. Calc.,%: C 70.99; H 10.00; N 8.87; S 6.77; found,%: C 70.58; H 10.32; N 8.78; S 6.75;
7	77	203-204°C i-PrOH: water 1: 1	<sup>1</sup> H NMR δ (ppm): 0.83 t (J = 7.2), 1.24 s (30H), 1.35 s (18H, t-Bu), 2.16 t (J = 7.3, 2H, CH <sub>2</sub> ), 2.37 s (2H, CH <sub>2</sub> ), 2.63 s (2H, CH <sub>2</sub> ), 6.65 s (1H, OH), 6.67 s (2H, Har), 7.05 d (J = 8.1, 2H, Har), 7.29 d (J = 8.2, 2H, Har). MS: (M +) m / z 689. Calc,%: C 74.84; H 9.79; N 6.09; S 4.65; Found,%: C 74.69; H 9.95; N 6.14; S 4.49;
8	55	155-157 °C EtOH:water 1:1	<sup>1</sup> H NMR (ppm): 11.37 (18H, s, t-Bu), 2.86 (4H, s, CH <sub>2</sub> -CH <sub>2</sub> ), 5.52 (2H, s, NH <sub>2</sub> ), 6.75 (1H, s, OH), 6.93 s (2H, s, Har), 13.46 (1H, s, NH). <sup>13</sup> C NMR (DMSO d <sub>6</sub> , δ): 166.15, 151.99, 139.59, 131.65, 128.74, 124.78, 34.88, 31.98, 30.90, 27.13. MS: (M +) m/z 348. Calc. %: C: 62.03, H: 8.10, N: 16.08, S: 9.20. Found: C: 62.21, H: 8.25, N: 16.01, S: 9.11.
9	43	71-73 °C benzene: hexane 1: 1	1.23 (18H, s, t-Bu), 2.98 (2H, t, J = 7.4, CH <sub>2</sub> -CH <sub>2</sub> ), 3.22 (2H, t, J = 7.2, CH <sub>2</sub> -CH <sub>2</sub> ), 6.71 (1H, s, OH), 6.78 (2H, s, Har). <sup>13</sup> C NMR (CDCl <sub>3</sub> , δ): 13.93, 22.56, 28.47, 28.88, 29.08, 29.34, 29.65, 30.29, 31.44, 31.91, 32.32, 33.07, 34.25, 124.88, 130.72, 136.06, 147.65, 152.28, 153.32, 169.53. MS: (M +) m/z 596. Calc.%: C: 72.43, H: 10.13, N: 9.39, S: 5.37. Found: C: 72.27, H: 10.31, N: 9.28, S: 5.32.
10	52	68-70 °C CHCl <sub>3</sub> : hexane 1:1	<sup>1</sup> H NMR δ (ppm): 0.85 (3H, s, CH <sub>3</sub> ), 1.26 (30H, s, -CH <sub>2</sub> -), 1.37 (18H, s, t-Bu), 2.98 (2H, t, J = 7.4, CH <sub>2</sub> -CH <sub>2</sub> ), 3.22 (2H, t, J = 7.2, CH <sub>2</sub> -CH <sub>2</sub> ), 6.74 (1H, s, OH), 6.82 (2H, s, Har). <sup>13</sup> C NMR (CDCl <sub>3</sub> , δ): 14.08, 22.66, 27.31, 28.47, 28.88, 29.06, 29.33, 29.52, 30.27, 31.42, 31.89, 32.29, 33.00, 34.28, 124.89, 130.45, 136.09, 147.66, 152.35, 153.67, 170.43. MS: (M +), m/z 568. Calc.%: C: 71.78, H: 9.92, N: 9.85, S: 5.64. Found: C: 71.62, H: 10.07, N: 9.78, S: 5.58.4.

**Table 2.** The antioxidant activity test results of the obtained substances.

Property	Agidol-1	4	6	7	9	10
Viscosity rel. change, %	24,2	23,36	51,19	-4,13	12,6	18,12
D CO, rel. un.	0,120	0,366	0,16	0,004	0,156	0,109

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