Inhibited Oxidation of Hydrocarbons in the Presence of Nitrogen, Phosphorus, Selenium, and Sulfur-Containing Heterocyclic Compounds

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ABSTRACT: *With the expansion of the scope of lubricant oils and fuels, the requirements for their performance properties are increasing. One of the performance characteristics of these petroleum products is their oxidation resistance. It is known that as a result of oxidation, their performance properties deteriorate. Antioxidant stabilizers are used to increase the resistance of organic materials against oxidation. The study of the mechanism of action of oxidation inhibitors is one of the most important tasks in this field, the solution of which is the creation of a theoretically substantiated approach to the targeted synthesis of more effective antioxidants. To create the theoretical and practical foundations of solving this problem was to find novel classes of effective additives of multivalent activity, particularly antioxidants, a series of recently synthesized nitrogen, sulfur, selenium and phosphorus polyfunctional compounds, including pyrroledithioates, 6,8-bicycloctanes, aminopyrimidine, tris(2-pyridyl)phosphinesulfide and -selenide have been investigated using model oxidative reactions. The compounds studied appear to be perspective inhibitors of hydrocarbon oxidation. Some of them are antioxidants of combined action, breaking the chains of the oxidative reactions with cumene peroxide radicals and catalytically decomposing cumene hydroperoxide.*

KEYWORDS: *Pyrrole; Phosphine; Selenide; Cumene; Antioxidant; Mechanism; Kinetics*.

INTRODUCTION

The rapid development of technology has toughened requirements for the exploitation of oil products (lubricants, fuels) used throughout the year [1-2]. In this connection, the targeted synthesis of the new generation of more efficient organic compounds, antioxidants, and other functional additives is one of the actual problems that dramatically improves the oil properties exploitation properties (oxidation, friction, corrosion). From this point of view, the new and more effective antioxidant, antimicrobial additives for lubricant oxidation, non-sprinkling and lubrication, antimicrobial additives and their effects on lubricants, interactions of additives, and physicochemical properties,

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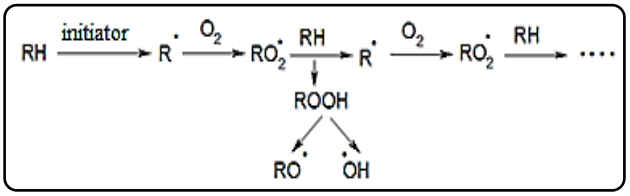


their effectiveness, effects of additives, and other theories chemistry researchers are required to study, substantiate, and deepen the issues deeper and deeper, as and theoretical basis for the synthesis of new additives.

One of the most important problems of the modern science of heathology is to protect the oxidation process from exploitation, fatigue, and other oil products exploitation or prolonged storage. Antioxidant additives are used to protect the fuels and lubricants from oxidation. At present, the active ingredient is alkylphenols, amines, aminophenols, various sulphides, diatomaceous acid salts, and the like [3-4].

The oxidation of hydrocarbons is known to be a radical-chain and degenerate-branched process, which simply can be represented as follows:

To inhibit this process, one should employ the compounds that would quickly react with the forming radicals (R^* or RO_2^*) or destroy the hydroperoxide without generating other free radicals.

Since the antioxidant properties of additives are due to the presence of certain functional groups in their composition, the investigations into the synthesis and mechanism of the antioxidant action of organic compounds containing two or more functional groups in the molecule, which allow combining various types of antioxidants in one structure, is of undoubted research and practical interest.

The obtained extensive kinetic and chemical information on the mechanism of action of polyfunctional antioxidants in various oxidizing systems is the scientific basis for targeted synthesis and preparation of antioxidant compositions in relation to specific systems, taking into account the specifics of their oxidative degradation.

The literature publishes a large number of scientific and research works that provide anti-oxidant properties of nitrogen and sulfur-containing compounds. The object of the research was to use sulphides, dithiophosphate, xanthogenate, heterocysts from different sulfur (phenothiazine, benzthiazole, etc.). However, antioxidant properties of alkilrodaides, triazines, and amintiols, which have been found to contain up to date conditions, have been studied less [5-7].

In the present work, we have studied a series of recently synthesized, earlier unknown nitrogen, sulfur, selenium, and phosphorus polyfunctional compounds, including pyrrolecarbodithi-oates, 6,8-bicycloctanes, aminopyrimidine, tris(2-pyridyl)phosphinesulfide and –selenide as potential polyfunctional multivalent fuel additives. The mechanism of their action was investigated and the relationship between structure and efficiency of their antioxidant activity was estimated.

When selecting compounds for the study, it was assumed that the molecules should combine the properties of two types of antioxidants. The first one should effectively break the oxidation chains via the reaction with peroxide radicals, and the second one should decompose hydroperoxides. As is known, the first type of antioxidants includes mainly phenols and aromatic amines, and the second type consists of sulfur-containing compounds.

RESULTS AND DISCUSSION

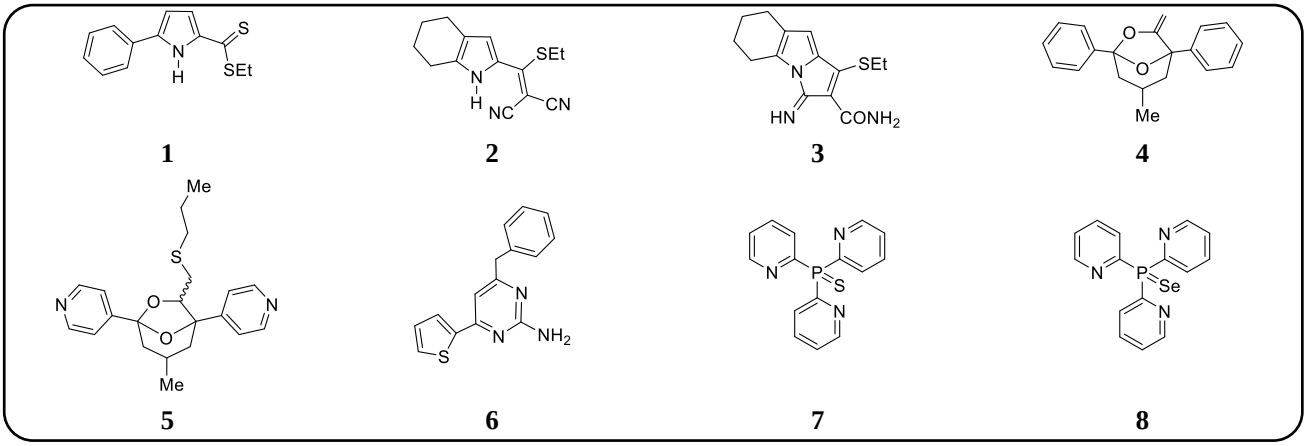
Chemistry

For the study, we have chosen eight representatives of the recently synthesized classes of nitrogen, sulfur, selenium, and phosphorus compounds (1–8) as the antioxidants of combined action (Scheme 1).

All compounds are synthesized by original straightforward methods from available starting materials. When selecting the compounds for the study, we consider that if some of them would show promising performance characteristics, the synthetic procedures might be easily scaled up.

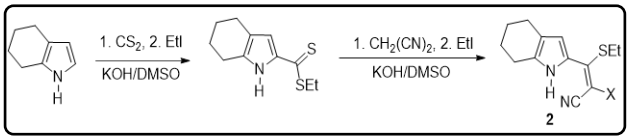
5-Phenylpyrrole-2-carbodithioate (1) was chosen to take into account the known sensitivity of pyrroles to oxidizers, on the one hand [8], and the antioxidant activity of sulfide and thiocarbonyl fragments, on the other hand. For the same reasons, pyrrole compounds (2) (2,2-dicyanoethenyl-4,5,6,7-tetrahydroindole) and (3) (3-imino-1-ethylsulfanyl-5,6,7,8-tetrahydro-3*H*-pyrrolo[1,2-a]indole-2-carboxamide) were selected for containing divalent sulfur atoms, functional groups, and exo- and endocyclic double bonds sensitive to radical attack.

Bridgehead bicyclic acetal, 6,8-dioxamethylenebicyclooctane (4) (3-methyl-7-methylene-1,5-diphenyl-6,8-dioxabicyclo[3.2.1]octane) contains an

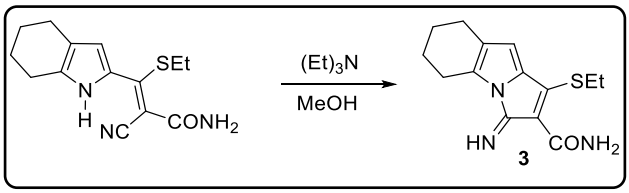


Scheme 1: Synthesized compounds (1-8)

Scheme 2: Synthesis of 5-phenylpyrrole-2-carbodithioate (1)



Scheme 3: Preparation of 2,2-dicyanoethenyl-4,5,6,7-tetrahydroindole (2)



Scheme 4: Synthesis of 3-imino-1-ethylsulfanyl-5,6,7,8-tetrahydro-3H-pyrrolo[1,2-a]indole-2-carboxamide (3)

extremely reactive exocyclic double bond, which is capable [9] of serving as a trap for radicals and protons. The related structure (5) (3-methyl-7-((propylthio)methyl)-6,8-dioxabicyclo[3.2.1]octane-1,5-diyl)dipyridine), bearing sulfide and pyridine substituents, could exhibit antioxidant properties owing to oxidation of the sulfur and pyridine nitrogen atom to afford the corresponding sulfoxides, sulfones and pyridine-N-oxides [10].

It was expected that the thiophene-aminopyrimidine ensemble (6) (4-benzyl-6-(thiophen-2-yl)pyrimidin-2-amine) would be able to exhibit antioxidant properties due to its potentially high and multifaceted chemical activity.

Tris-(2-pyridyl)phosphine sulfide (7) and tris-(2-pyridyl)phosphine selenide (8) were supposed to be antioxidants of combined action owing to the high ability of oxidizing the P=S and P=Se bonds [11], as well as potential oxidation of the pyridine fragments.

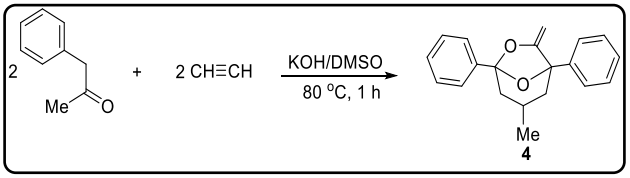
In addition, the choice of these compounds is because they possess a high physiological activity, suppressing various pathological processes occurring in living organisms [12-15]. Since most of these processes, like the oxidation of hydrocarbons, involve free radicals, we assumed that these compounds would also inhibit the oxidation of hydrocarbon fuels.

The method for the synthesis of 5-phenylpyrrole-2-carbodithioate (1) is based on the reaction of available [16] 2-phenylpyrrole with carbon disulfide in the super-basic system KOH-DMSO followed by ethylation of potassium pyrrole-2-carbodithioate with ethyl iodide (Scheme 2):

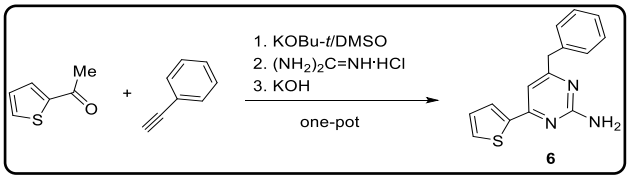
2,2-Dicyanoethenyl-4,5,6,7-tetrahydroindole (2) is synthesized by the treatment of the corresponding carbodithioate, prepared according to the same procedure shown in Scheme 2 from 4,5,6,7-tetrahydroindole, with malononitrile in the system KOH-DMSO system followed by ethylation of the potassium intermediate with ethyl iodide (Scheme 3):

The synthesis of 3-imino-1-ethylsulfanyl-5,6,7,8-tetrahydro-3*H*-pyrrolo[1,2-*a*]indole-2-carboxamide (3) is carried out by intramolecular cyclization of 2-carbamoyl-2-cyanoethenyl-4, 5,6,7-tetrahydroindole (Scheme 4):

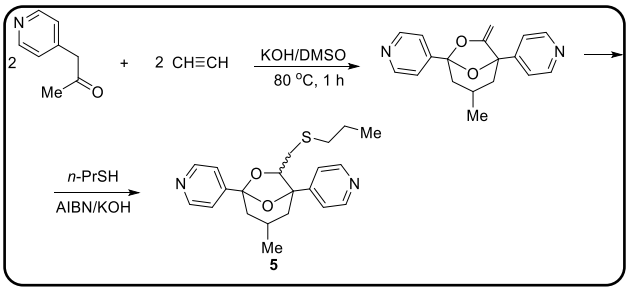
The one-pot assembly of 3-methyl-7-methylene-1,5-diphenyl-6,8-dioxabicyclo[3.2.1]octane (4) is implemented from two molecules of acetylene and two molecules of acetophenone in the super basic system KOH-DMSO [17] (Scheme 5) :



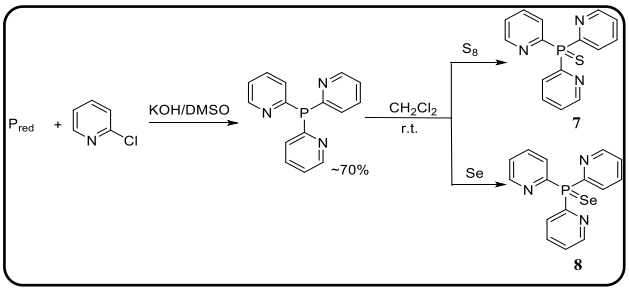
Scheme 5: Preparation of 3-methyl-7-methylene-1,5-diphenyl-6,8-dioxabicyclo[3.2.1]octane (4)



Scheme 7: Preparation of 4-benzyl-6-(thiophen-2-yl)pyrimidine -2-amine (6)



Scheme 6: Synthesis of 3-methyl-7-((propylthio)methyl)-6,8-dioxabicyclo[3.2.1]octane-1,5-diyl)dipyridine (5)



Scheme 8: Synthesis of tris-(2-pyridyl)phosphine sulfide (7) and –selenide (8)

The corresponding bridgehead heterocycle with an exocyclic methylene group and two pyridine substituents [18], assembled in a one-pot manner from two molecules of acetylene and two molecules of acetylpyridine, is treated with propylmercaptan in the presence of a radical initiator (AIBN) and potassium hydroxide [19]) to furnish 3-methyl-7-((propylthio)methyl)-6,8-dioxabicyclo[3.2.1] octane-1,5-diyl)dipyridine (5) (Scheme 6).

4-Benzyl-6-(thiophen-2-yl)pyrimidine-2-amine (6) is obtained from 2-acetylthiophene, phenylacetylene and $(NH_2)_2C$=NH·HCl [20] (Scheme 7).

Tris-(2-pyridyl)phosphine sulfide (7) and –selenide (8) are prepared from *tris*(2-pyridyl)phosphine and elemental sulfur and selenium. *Tris*-(2-pyridyl)phosphine is obtained by the procedure described in the literature [21-22] from red phosphorus and 2-chloropyridine in the superbasic system KOH/DMSO (Scheme 8):

Antioxidant activity

The study of cumene auto-oxidation in the presence of compounds (1-8) has shown that they effectively inhibit this process. The kinetic curves of auto-oxidation at 110 °C in the presence of compounds (1-8) are shown in Fig. 1, and the values of auto-oxidation induction period are given in Table 1.

To establish the mechanism of the antioxidant action of the synthesized compounds, the kinetics of their reaction with cumene peroxide radicals and cumene hydroperoxide (CHP) has been investigated.

In order to evaluate the ability of the studied compounds (1-8) to break the oxidation chains via the reaction with cumene peroxide radicals, the oxidation of cumene was initiated by azodiisobutyronitrile (AIBN) at 60 °C in the presence of these inhibitors. In all experiments, the concentration of the initiator was $2*10^{-2}$ mol/l, and the content of the inhibitor was $5*10^{-4}$ mol/l. It was found that all studied compounds, to one degree or another, inhibited the initiated oxidation of cumene (Fig. 2):

Using the value of the induction time (τ) of the initiated cumene oxidation, the stoichiometry coefficient f was calculated. The latter is equal to the number of oxidation chains breaking under the action of one inhibitor molecule and products of its conversion:

$$f = \frac{\tau W_i}{[InH]_0} \quad (1)$$

where $\tau_{ind.}$ is induction time, W_i is initiation rate, $[InH]_0$ is initial concentration of the inhibitor.

To determine the value of the rate constant of the interaction of inhibitor with cumene peroxide radicals (κ_7), the kinetic curves of the initiated oxidation of cumene were transformed from $\Delta[O_2]$-τ coordinates to $\Delta[O_2]^{-1}$-τ^{-1} coordinates. Using the slope of the straight line

$$\mathrm{tg}\,\alpha = \frac{f k_7 [InH]_0}{(k_2[RH]W_i)} \quad (2)$$

it was found that

$$k_7 = \frac{tg\alpha k_2 [RH] W_i}{f.[InH]_0} \quad (3)$$

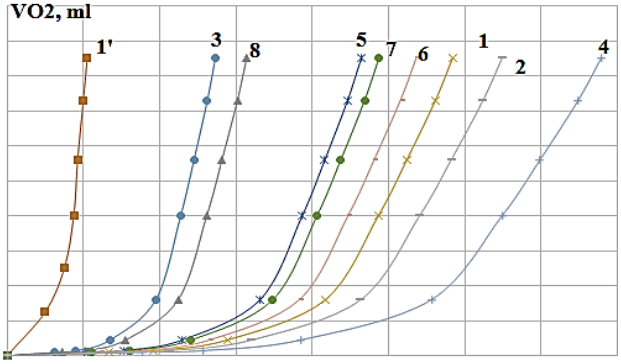


Fig. 1: Kinetic curves of cumene auto-oxidation in the presence of the synthesized com pounds: T = 110˚C, V_{O2} is a volume of oxygen (mL), τ is a time (min); [InH]= 0 (1^{I}) [InH]= 1-2-3-4-5-6-7-8 = $5 \cdot 10^{-4}$ mol/l.

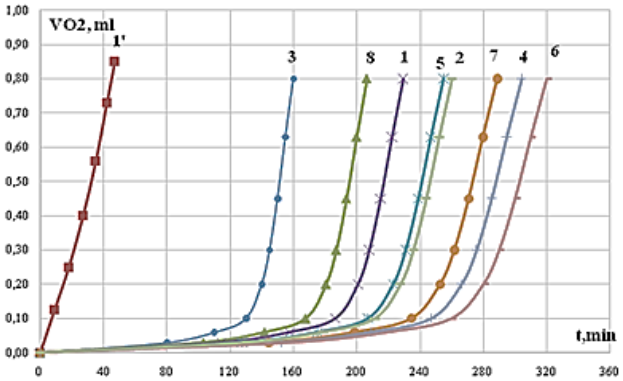


Fig. 2: Kinetic curves of initiated cumene oxidation in the presence of synthesized compounds 1-8: T = 60°C; V_{O2} is the volume of oxygen (mL), τ is the time (min.), [InH]=0 (1') [InH]=$5 \cdot 10^{-4}$ mol/l = 1-8.

where: k_2=1,51 1/mol.s, [RH]=7,17 1/mol.s

The values of the kinetic parameters of the reaction of the synthesized compounds with cumene peroxide radicals are given in Table 1.

To evaluate the ability of the synthesized compounds 1-8 to decompose CHP, the reaction of cumene hydroperoxide with inhibitors has been implemented at 110 °C in chlorobenzene under nitrogen atmosphere (at this temperature, CHP is thermally stable). The studies have shown that the inhibitors, which contain a sulfur atom in the molecule, effectively decompose CHP (Fig. 3).

Moreover, one molecule of the studied inhibitors is capable of decomposing several thousand CHP molecules, that is, the reaction has a catalytic character.

The number of CHP molecules (ν), decomposed under the action of one molecule of the studied compounds, was calculated by the formula:

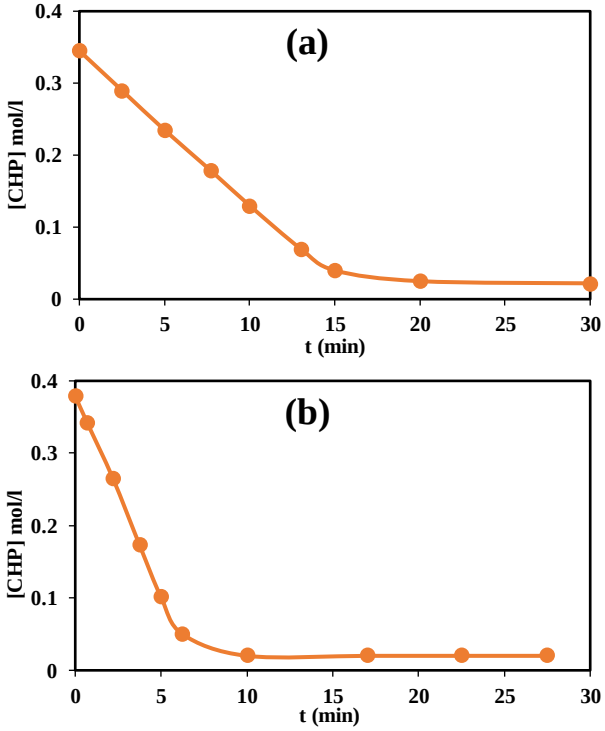


Fig. 3: Kinetic curves of decomposition of CHP (a) under the action of compound 7 [InH]$_{(IV)}$=5.10^{-4} mol/l at110˚C, initial concentration of [CHP] = 0.34 mol/l, τ is time (min). (b) under the action of compound 1 [InH]$_{(IV)}$=5.10^{-4} mol/l at 110˚C, initial concentration of [CHP] = 0.37 mol/l, τ is time (min).

$$\nu = \frac{[CHP]_0 - [CHP]_\infty}{[InH]_0} \quad (4)$$

where $[CHP]_0$ and $[CHP]_\infty$are initial and final concentration of CHP, respectively;$[InH]_0$is initial concentration of the antioxidant.

It is found that for all compounds, the reaction with CHP is of the first order both in terms of antioxidant and CHP, and the initial reaction rate of the catalytic decomposition of CHP follows the equation:

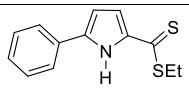
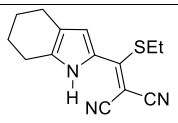
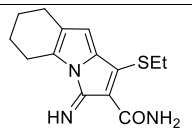
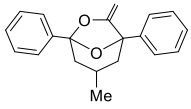
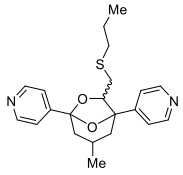
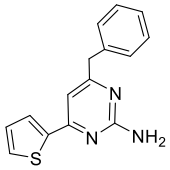
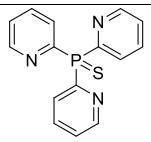
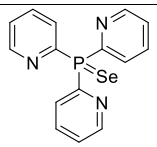
$$w_0 = K\,[InH]_0 * [CHP] \quad (5)$$

The values of the rate constant of CHP decomposition under the action of the studied compounds (K) and catalytic factor (ν) are given in Table 1.

The Table also contains values of the induction time (τ) of cumene autooxidation in the presence of the synthesized compounds, as well as the kinetic parameters of their reaction with cumene peroxide radicals and cumeme hydroperoxide.

As shown in Table 1, all the studied compounds, except for compound (3), exhibit quite high antioxidant properties

Table 1: The values of the induction time of cumene autooxidation in the presence of the synthesized compounds (1-8), as well as the kinetic parameters of their reaction with cumene peroxide radicals and cumene hydroperoxide

Compound	Formula	Induction time of cumene autooxidation (T=110°C), τ, min	Reaction with RO_2^* (T=60°C)		Reaction with CHP (T=110°C)	
			F	$K_7.10^{-4}$ l/mol·s	K, l/mol·s	ν
1		250	2.6	3.6	15	12000
2		220	2.2	3.2	13	10000
3		130	1.59	1.92	8	6000
4		210	1.81	2.88	-	-
5		260	2.73	3.84	6	4500
6		280	4.24	4.32	10	7000
7		200	1.97	3.12	11	8000
8		170	1.72	2.04	-	-
Ionol		150	2.10	2.00	-	-

and surpass the well-known antioxidant like ionol (2,5-di-tert-butyl-4-methylphenol) in terms of antioxidant activity.

Compounds (5, 6) and (1) possess the highest antioxidant activity. The latter is likely due to the fact that these compounds suppress peroxide radicals and very effectively break the oxidation chains. Also, unlike ionol, they efficiently decompose hydroperoxides into molecular products. In the reaction with peroxide radicals, the stoichiometry coefficient (f) for these compounds is ~4, i.e. one molecule of these compounds breaks about four oxidation chains, while one molecule of ionol breaks only 2 oxidation chains. The reaction rate constant with peroxide radicals for these compounds is also higher than that for ionol.

EXPERIMENTAL PART

Measurements

IR spectra were recorded in KBr pellets or film on a Bruker JFS-25 spectrometer in the 400–4000 cm^{-1} region. ^{1}H, ^{13}C, ^{15}N, ^{31}P and ^{77}Se NMR spectra were recorded

at room temperature on a Bruker-DPX-400 instrument with an operating frequency of 400.13 (^{1}H), 100.62 (^{13}C), 40.5 (^{15}N), 162.0 (^{31}P), 77.0 (^{77}Se) MHz, the solvent is DMSO-d6 and $CDCl_3$. ^{1}H and ^{13}C NMR chemical shifts were recorded relative to residual solvent signals ($CDCl_3$, δ 7.27 and 77.0 ppm, respectively, or DMSO, δ 2.50 and 39.5 ppm, respectively). Elemental analysis was performed on a Flash EA 1112 Series analyzer.

Synthesis of sulfur-containing pyrroles 1-3

Ethyl 5-phenyl-1H-pyrrole-2-carbodithioate (1)

A mixture of 2-phenylpyrrole (1.43 g, 10 mmol) and $KOH{\cdot}0.5H_2O$ (1.30 g, 20 mmol) in DMSO (20 mL) was stirred for 30 min and carbon disulfide (1.52 g, 20 mmol) was added. The reaction mixture was allowed to stand at room temperature for 2 h, and then ethyl iodide (1.56 g, 10 mmol) was added. The reaction mixture was stirred for 2 h, then diluted with water (40 mL) and extracted with diethyl ether. After removing the solvent, the residue was passed through a column (Al_2O_3, hexane-diethyl ether, 1:1) to obtain 0.2 g of diethyl disulfide; 0.7 g (24%) of ethyl 5-phenyl-1*H*-pyrrole-1-carbodithioate and 1.46 g (59%) of the target ethyl 5-phenyl-1*H*-pyrrole-2-carbodithioate as yellow crystals, mp 67-68 °C. ^{1}H NMR (400 MHz, ДМСО-d_6), δ: 11.79 (s, 1H, NH), 7.93-7.91 (m, 2H, H_o Ph), 7.44-7.42 (m, 2H, H_m Ph), 7.34-7.33 (m, 1H, H_p Ph), 7.19 (*J* = 3.6, 2.4 Hz, H-3 pyrrole), 6.79 (*J* = 3.6, 2.6 Hz, H-4 pyrrole), 3.33 (q, *J* = 7.5 Hz, 2H, SCH_2), 1.30 (t, *J* = 7.5 Hz, Me) ppm. ^{13}C NMR (101 MHz, DMSO-d_6), δ: 206.0 (C=S), 141.8 (C-*i*), 140.5 (C-5), 130.8 (C-2), 129.0 (C-*m*), 128.6 (C-*p*), 126.3 (C-*o*), 115.0 (C-4), 110.6 (C-3), 28.6 (SCH_2), 13.5 (Me) ppm.

2-[(Ethylsulfanyl)(4,5,6,7-tetrahydro-1H-indol-2-yl)methylene]malononitrile (2)

Malonodinitrile (0.99 g, 15 mmol), $KOH{\cdot}0.5H_2O$ (0.98 g, 15 mmol) and DMSO (50 mL) were stirred at room temperature for 0.5 h, then ethyl 4,5,6,7-tetrahydroindole-2-carbodithioate (2.25 g, 10 mmol) and the mixture was heated at 108-110 °C for 1.5 h. The reaction mixture was diluted with water (1:3), the resulting crystals were filtered and dried to give 2.26 g (88%) of 2-[(ethylsulfanyl)(4,5,6,7-tetrahydro-1*H*-indol-2-yl)methylene]malononitrile, mp 138-139 °C (methanol). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 11.81 (s, 1H, NH), 6.93 (d, *J* = 1.8 Hz, 1H, H-3), 3.05 (q, *J* = 7.4 Hz, 2H, SCH_2), 2.67-2.66 (m, 2H, CH_2-7), 2.50-2.49 (m, 2H, CH_2-4), 1.74-1.73 (m, 2H, CH_2-6), 1.69-1.68 (m, 2H, CH_2-5), 1.18 (t, *J* = 7.4 Hz, 3H, Me) ppm. ^{13}C NMR (101 MHz, DMSO-d_6), δ: 159.3 (=C-SEt), 141.6 (C-5), 126.1 (C-2), 124.8 (C-4), 120.8 (C-3), 116.6 (CN), 115.5 (CN), 68.2 [=$C(CN)_2$)], 31.2 (SCH_2), 23.5 (CH_2-7), 23.0 (CH_2-5), 22.7 (CH_2-6), 22.4 (CH_2-4), 14.6 (SCH_2Me) ppm.

3-Imino-1-ethylsulfanyl-5,6,7,8-tetrahydro-3H-pyrrolo[1,2-a]indole-2-carboxamide (3)

A solution of 2-cyano-3-(ethylsulfanyl)-3-(4,5,6,7-tetrahydro-1*H*-indol-2-yl)acrylamide (0.55 g, 2 mmol) in methanol (10 mL) was heated in the presence of triethylamine (2-3 drops) for 10 h and cooled to room temperature. The resulting crystals were filtered off, washed with diethyl ether and dried to give 3-imino-1-ethylsulfanyl-5,6,7,8-tetrahydro-3*H*-pyrrolo[1,2-*a*]indole-2-carboxamide (0.25 g, 46%), mp 190-192 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 8.51 (s, 1H, $CONH_2$), 7.76 (s, 1H, =NH), 6.16 (s, 1H, pyrrole), 5.42 (s, 1H, $CONH_2$), 3.19 (q, *J* = 7.2 Hz, SCH_2), 2.72-2.70 (m, 2H, CH_2-7), 2.47-2.45 (m, 2H, CH_2-4), 1.90-1.88 (m, 2H, CH_2-5), 1.78-1.76 (m, 2H, CH_2-6), 1.43 (t, *J* = 7.2 Hz, Me) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ: 165.15 (CO), 157.79 (C-1), 155.58 (C-3), 131.21 (C-4), 129.45 (C-7), 125.93 (C-5), 113.91 (C-6), 112.76 (C-2), 26.2 (SCH_2), 22.9, 22.7, 22.2, 22.1 (CH_2-4-7), 14.3 (SCH_2Me) ppm.

Synthesis of 6,8-dioxabicyclo[3.2.1]octanes (4-5)

3-Methyl-7-methylene-1,5-diphenyl-6,8-dioxabicyclo[3.2.1]octane (4)

A mixture of acetophenone (2.00 g, 16.6 mmol) and KOH $0.5H_2O$ (1.08 g, 16.6 mmol) in DMSO (50 mL) was placed into a 0.25-l steel rotating autoclave. The latter was fed with acetylene under pressure of 14 atm and then decompressed to atmospheric pressure to remove air. The autoclave was fed with acetylene again (initial pressure at ambient temperature was 14 atm, which reached a maximum of 27 atm at the reaction temperature and then dropped upon acetylene consumption during the reaction) and heated (80 °C) upon rotating for 1 hour. The reaction mixture, after cooling to room temperature, was diluted with cool (7-10 °C) water (100 mL) and extracted with diethyl ether (20 mL x 5). The obtained organic extract was washed with water (20 mL x 3) and dried (K_2CO_3) overnight. After removal of the extractant, 2.46 g

of a crude residue was obtained. Column chromatography (basic Al_2O_3, hexane:diethyl ether 3:1) gave 2.10 g (86%) of compound (**4)** as yellow oil. Found: C, 82.18; H, 6.97%. Calcd. for $C_{20}H_{20}O_2$ (292.38): C, 82.16; H, 6.89%. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.68-7.66 (m, 2H, HPh), 7.60-7.58 (m, 2H, HPh), 7.45-7.31 (m, 6H, HPh), 4.29 (d, 1H, *J* = 2.3 Hz, Hb), 3.56 (d, 1H, *J* = 2.3 Hz, Ha), 2.49 (m, 1H, H-4), 2.41 (m, 1H, CH-Me), 2.31 (m, 1H, H-2), 1.75 (m, 1H, H-4'), 1. 66 (m, 1H, H-2'), 1.11 (d, 3H, *J* = 6.2 Hz, Me) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ: 163.2 (C-7), 140.0 (C-*i*), 139.5 (C-*i'*), 128.9 (C-*p*), 128.3 (C-*m*, C-*m'*), 128.2 (C-*p'*), 126.0 (C-*o*), 125.4 (C-*o'*), 108.8 (C-5), 85.5 (C-1), 78.4 (=CH_2), 42.3, 40.9 (C-2, C-4), 25.4 (C-3), 21.4 (Me) ppm. IR (film), ν: 3289, 2956, 2970, 2808, 1729, 1682, 1381, 1337, 1275, 1146, 1129, 1114, 1061, 1026, 1012, 986, 827, 761, 698 cm^{-1}.

3-Methyl-7-((propylthio)methyl)-6,8-dioxabicyclo[3.2.1] octane-1,5-diyl)dipyridine (5)

To a mixture of KOH·0.5H_2O (0.065 g, 1 mmol) and *n*-propylthiol (4.57 g, 60 mmol) were added a 7-methylene-6,8-dioxabicyclo[3.2.1]octane (0.589 g, 2 mmol) and AIBN (1 mol%). The mixture was heated (65 °C) and stirred at 65 °C until the consumption of starting bicyclooctane (30 h, monitored by ^{1}H NMR spectroscopy after 4 hours, for every 2 additional hours, 1 mol% AIBN was added to the reaction mixture). The excess thiol was removed under reduced pressure to a cooled trap. The crude product was purified by flash column chromatography (silica gel, benzene). The compound **5** was obtained as colorless oil; yield 0.496 g (67%). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 8.67–8.63 (m, 2 H), 8.62–8.60 (m, 2 H), 7.53–7.48 (m, 2 H), 7.38–7.36 (m, 2 H, Py), 3.99 (dd, ^3J = 9.2 Hz, ^3J =3.6 Hz, 1 H, H-7), 3.07 (dd, ^2J = 13.5 Hz, ^3J = 9.2 Hz, 1 H), 2.73 (dd, ^2J = 13.5 Hz, ^3J = 3.6 Hz, 1 H, SCH_2C-7), 2.58–2.37 (m, 4 H, H-3, H-4_{eq}, $CH_2C\underline{H}_2S$), 2.10 (dd, ^2J = 13.4 Hz, ^3J = 5.7 Hz, 1 H, H-2_{eq}), 1.62–1.49 (m, 4 H, H-2_{ax}, H-4_{ax}, Me$C\underline{H}_2$), 1.06 (d, ^3J = 6.5 Hz, 3 H, 3-Me), 0.92 (t, ^3J = 7.3 Hz, 3 H, $\underline{Me}CH_2$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ: 150.3, 150.1, 149.2, 148.6, 120.2, 120.0 (10 C of Py), 107.1 (C-5), 86.4 (C-7), 84.2 (C-1), 43.1 (C-4), 36.9 (C-2), 34.9, 30.1 (CH_2SCH_2), 25.4 (C-3), 22.8 (MeCH_2), 21.9 (3-Me), 13.5 (MeCH_2) ppm. IR (film), ν: 3029, 2958, 2925, 2871, 1686, 1601, 1555, 1456, 1410, 1379, 1353, 1321, 1296, 1246, 1180, 1163, 1143, 1119, 1070, 1035, 1008, 993, 953, 940, 912, 874, 847, 816, 674, 668, 663, 652 cm^{-1}.

The inisial 3-methyl-7-methylene-6,8-dioxabicyclo[3.2.1]octane-1,5-diyl)dipyridine was prepared according to [18].

Preparation of thiophene-aminopyrimidine (6)

4-Benzyl-6-(thiophen-2-yl)pyrimidin-2-amine (6)

A mixture of 2-acetylthiophene (0.631 g, 5 mmol), phenylacetylene (0.510 g, 5 mmol) and KOBu-t (0.673 g, 6 mmol) in DMSO (10 mL) was heated (100 °C) and stirred at 100 ^{0}C for 30 min. After cooling (70 °C), H_2O (0.090 g, 5 mmol) and $(NH_2)_2C{=}NH_2Cl$ (0.573 g, 6 mmol) were added to the reaction mixture and stirred at 70 °C for 0.5 h. Then, KOH 0.5 H_2O (0.325 mg, 5.0 mmol) was added and the mixture was stirred at 70 °C for 30 min. After cooling (rt), the reaction mixture was diluted with H_2O (15 mL), neutralized with NH_4Cl and extracted with $CHCl_3$ (10 mL × 4). The organic extract was washed with H_2O (5 mL × 3) and dried ($MgSO_4$). $CHCl_3$ was evaporated in vacuum and the residue was purified by column chromatography (Al_2O_3, eluent C_6H_6/Et_2O with a gradient from 1:0 to 10:1). 4-Benzyl-6-(thiophen-2-yl)pyrimidin-2-amine was isolated as a cream-colored solid (0.401 g, 30%); mp 180-185°C. Found: C, 67.37; H, 4.91; N, 15.62; S, 11.94%. Calcd. for $C_{15}H_{13}N_3S$ (267.35): C, 67.39; H, 4.90; N, 15.72; S, 11.99%. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 3.93 (s, 2H, $C\underline{H}_2Ph$), 5.05 (s, 2H, NH_2), 6.72 (s, 1H, H-5), 7.06 (d, *J* = 3.8, 5.0 Hz, 1H, H-9), 7.20-7.42 (m, 5H, H-*o,m,p*), 7.41 (d, *J* = 5.0 Hz, 1H, H-10), 7.57 (d, *J* = 3.8 Hz, 1H, H-8) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ: 44.2 ($\underline{C}H_2Ph$), 105.4 (C-5), 126.8 (C-*p*), 127.0 (C-8), 128.1 (C-9), 128.7 (C-*m*), 129.2 (C-10), 129.3 (C-*o*), 138.0 (C-*i*), 143.0 (C-7), 160.3 (C-6), 163.2 (C-4), 170.9 (C-2) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$), δ: −136.6 (N-3), −148.3 (N-1), −305.6 (NH_2) ppm. IR (KBr), ν: 3485, 3289, 3166, 3100, 3083, 3028, 2920, 1622, 1573, 1556, 1548, 1518, 1494, 1459, 1446, 1416, 1366, 1342, 1227, 1194, 1172, 1074, 1044, 1030, 908, 862, 839, 826, 791, 736, 728, 707, 622, 608, 577, 568, 520 cm^{-1}.

Synthesis of tris-(2-pyridyl)phosphine sulfide (7) and tris-(2-pyridyl)phosphine selenide (8)

Tris-(2-pyridyl)phosphine sulfide (7)

Tris-(2-pyridyl)phosphine (0.521 g, 2 mmol) was dissolved in dichloromethane (10 mL) and elemental sulfur (0.064 g, 2.01 mmol) was added. The reaction mixture was stirred at room temperature for 2 h. The solution was filtered and the solvent was removed. A white crystalline product (0.56 g, 95%) was crystallized from

iso-propanol and dried in air; mp = 158-160°C (*i*-PrOH); ref. [19] 160 °C ($CHCl_3$).[2] Found: C, 60.7; H, 4.0; N, 14.3; P, 19.1; S, 10.9 %. Calcd. for $C_{15}H_{12}N_3PS$ (297.32): C, 60.6; H, 4.1; N, 14.1; P, 19.4; S, 10.8 %. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.32 (3H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.2 Hz, $^5J_{HH}$ = 2.9 Hz, H-5), 7.77 (3H, $^3J_{HH}$ = 7.8 Hz, $^4J_{PH}$ = 4.6 Hz, $^4J_{HH}$ = 1.7 Hz, H-4), 8.25 (3 H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HP}$ = 6.5 Hz, $^4J_{HH}$ = 1.0 Hz, H-3), 8.70 (3 H, $^3J_{HH}$ = 4.8 Hz, H-6) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ: 124.90 (C-5, $^4J_{PC}$ = 3.3 Hz), 128.56 (C-3,$^2J_{PC}$ = 25.0 Hz), 136.04 (C-4,$^3J_{PC}$ = 10.2 Hz), 149.87 (C-6, $^3J_{PC}$ = 19.3 Hz), 155.05 (C-2, $^1J_{PC}$ = 114.6 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$), δ: 34.8 ppm. IR (KBr pellet), ν: 3037, 2986, 1571, 1449, 1419, 1279, 1235, 1208, 1161, 1051, 1131, 1085, 1042, 987, 774, 742, 731, 661, 614, 549, 519, 473, 438, 394 cm^{-1}.

Tris-(2-pyridyl)phosphine selenide (8)

Tris-(2-pyridyl)phosphine (0.521 g, 2 mmol) was dissolved in dichloromethane (10 mL) and elemental selenium (0.155 g, 2.01 mmol) was added. The reaction mixture was stirred at room temperature for 2 h. The solution was filtered and the solvent was removed. *Tris*-(2-pyridyl)phosphine selenide was obtained (0.65 g, 95%) as white powder; mp 175 °C (EtOH); ref. [22] 176-178 °C (EtOH). Found: C, 52.3; H, 3.5; N, 12.5; P, 9.1; Se, 22.9 %. Calcd. for $C_{15}H_{12}N_3PSe$ (318.18): C, 52.3; H, 3.5; N, 12.2; P, 9.0; Se, 22.9 %. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.31 (3H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 4.7 Hz, $^3J_{HH}$ = 3.1 Hz, $^4J_{HH}$ = 1.2 Hz, H-5), 7.79 (3 H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 1.8 Hz, H-4), 8.30 ddd (3 H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HP}$ = 6.8 Hz, $^4J_{HH}$ = 1.2 Hz, H-3), 8.69 br.d (3 H, $^3J_{HH}$ = 4.8 Hz, H-6) ppm. ^{13}C NMR (101 MHz, $CDCl_3$), δ: 124.88 (C-5, $^4J_{PC}$ = 3.2 Hz), 129.22 (C-3,$^2J_{PC}$ = 26.0 Hz), 136.17 (C-4,$^3J_{PC}$ = 10.5 Hz), 149.86 (C-6, $^3J_{PC}$ = 19.0 Hz), 154.12 (C-2, $^1J_{PC}$ = 106.0 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$), δ: 30.13 ($^1J_{PSe}$ = 732.6 Hz) ppm. ^{77}Se NMR (77 MHz, $CDCl_3$), δ: -307.2 ($^1J_{PSe}$ = 746.5 Hz) ppm. IR (KBr pellet), ν: 3063, 1566, 1449, 1420, 1282, 1124, 1050, 985, 772, 734, 560, 505, 450 cm^{-1}.

CONCLUSIONS

In conclusion, a specially selected range of nitrogen-, phosphorus-, selenium-, and sulfur-containing heterocyclic compounds, prespective multivalent effective antioxidants of new type, has been synthesized. The composition and structure of the compounds has been proved by mod-ern physical-chemical methods.

It is established that these compounds are effective inhibitors of hydrocarbon oxidation. The mechanism of their antioxidant action involves the breaking of the oxidation chains via the reaction with peroxide radicals, and (for some compounds) catalytic decomposition of hydroper-oxides into molecular products.

It has been established that nitrogen-, and sulfur-containing heterocyclic compounds can actively influence the oxidation of hydrocarbons.

This study revealed that the obtained extensive kinetic and chemical information on the mechanism of action of polyfunctional antioxidants in various oxidizing systems is the scientific basis for targeted synthesis and preparation of antioxidant compositions in relation to specific systems, taking into account the specifics of their oxidative degradation.

Received: Jul. 17, 2022 ; Accepted: Nov. 14, 2022

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