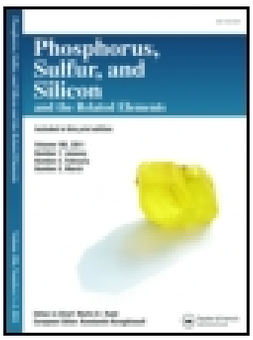

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Synthesis and antioxidant properties of bis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propyl)phosphite

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ABSTRACT

Bis(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl)phosphite was synthesized by reaction of 2,6-di-*tert*-butyl-4-(3-hydroxyproyl)phenol with dibutyl phosphite. The structure of bis(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl)phosphite was supported by IR and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy; its composition was confirmed by elemental analysis. High antioxidant activity of the synthesized phosphite has been shown in a model reaction with the free chromogen-radical 2,2-diphenyl-1-picrylhydrazyl and under conditions of accelerated thermal oxidation of paraffinic and mineral oils.

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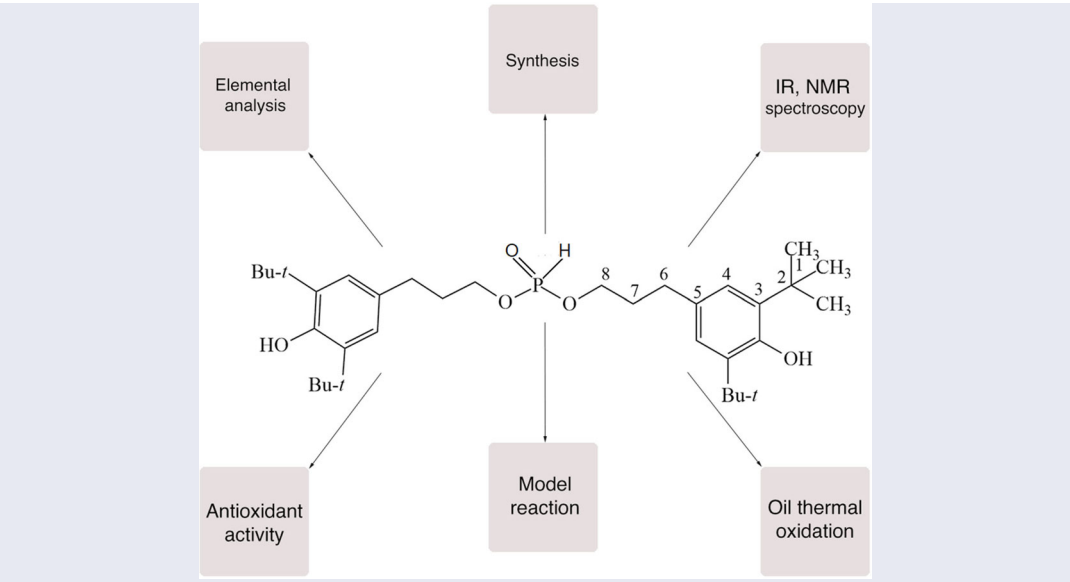
Bis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propyl)phosphite; synthesis; antioxidant properties; IR; NMR spectroscopy; 2,2-diphenyl-1-picrylhydrazyl; thermal oxidation

GRAPHICAL ABSTRACT



Introduction

Antioxidants that are capable to inhibit free-radical processes of oxidation of organic substances are widely used to extend the service life and improve the performance of polymeric and combustive-lubricating materials, to prevent oxidative deterioration of food products, as biologically active additives and as drugs.[1–4]

A modern approach to create effective antioxidants is the development of polyfunctional compounds which contain combinations of several reaction centers, which inhibit free radical chain oxidation processes simultaneously by different mechanisms: the acceptance of peroxide and alkyl radicals, the destruction of hydroperoxides without radical and the deactivation of metals of variable valence.

For example, dialkyl(aryl)phosphites are known as effective antioxidants that inhibit oxidation by catalytic destruction of polymer hydroperoxides and acceptance of peroxide radicals, as well as being an effective polymer's color stabilizer and as hindered phenols they are peroxide radical scavengers.[5]

Results and discussion

The interaction of 2,6-di-tert-butyl-4-(3-hydroxypropyl)phenol **2** with dibutyl phosphite **3** took place according to Scheme 1:

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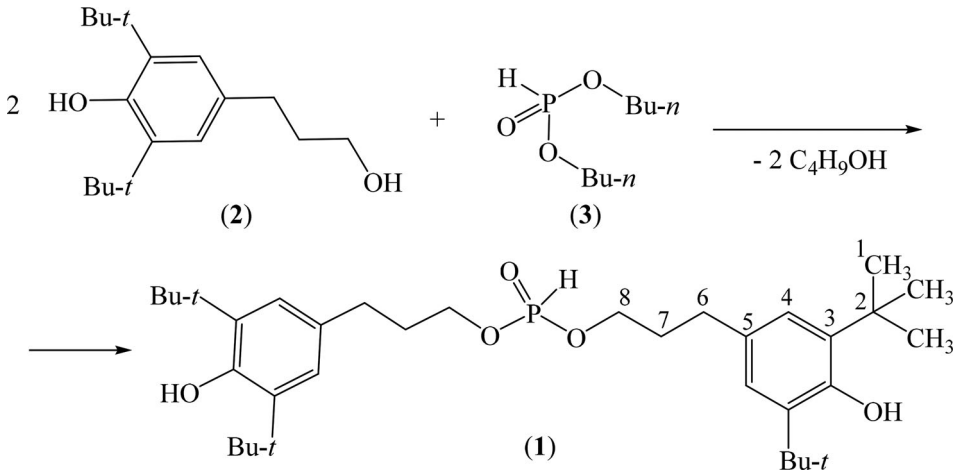


Scheme 1. Synthesis of phosphite **1**.

The characteristics correspond to the formation of bis(3-(3,5-di-*tert*-butyl-4-hydroxy-phenyl)propyl)phosphite **1**.

The antioxidant properties of the synthesized phosphite **1** were studied in a model reaction with the free chromogen-radical 2,2-diphenyl-1-picrylhydrazyl and under conditions of accelerated thermal oxidation of paraffinic and mineral oils. They were compared with those of the industrial phenolic antioxidants: 2,6-di-*tert*-butyl-4-methylphenol (Ionol), 4,4′-bis(2,6-di-tert-butylphenol) (Agidol-5) and pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate) (Irganox 1010).

The oxidation of paraffinic oil was evaluated by IR spectroscopy based on the rate of accumulation of carbonyl groups. The absorption band at 1721 cm^{-1} (D_1), corresponding to the stretching vibrations of the carbonyl group, was used as an analytical one. Band of 1470 cm^{-1} (D_2), caused by the deformation vibrations of the methyl and methylene groups, was used as an internal standard. The degree of paraffinic oil's oxidation with presence of additives was estimated by the ratio of optical densities D_1/D_2 (Figure 1).

The effectiveness of the antioxidants was defined under conditions of thermal oxidation of industrial oil (I40A). Accumulation of low molecular weight volatile acids (A_{lmw}), acid number (AN), and the amount of insoluble sludge in oil (m) were used as criteria (Table 1).

The obtained data (Figure 1, Table 1) show that the synthesized phosphite **1** has a high antioxidant activity. It significantly inhibits the thermal oxidation of paraffinic and mineral oils, reducing the amount of carbonyl compounds, volatile acids, and insoluble sludge in oils. By its antioxidant action, phosphite **1** surpasses the highly effective industrial antioxidants Irganox 1010, Ionol, and Agidol-5.

The interaction of the studied antioxidants with 2,2-diphenyl-1-picrylhydrazyl was carried out at 30 °C under pseudo-first order conditions of the radical in anhydrous 1,4-dioxane. In this solvent, the interaction of 2,2-diphenyl-1-picrylhydrazyl with antioxidant proceeds predominantly by the HAT (Hydrogen Atom Transfer) mechanism,[6] which consists in the homolytic separation of the hydrogen atom from the substance molecule (AH) and its transfer to 2,2-diphenyl-1-picrylhydrazyl (Scheme 2).

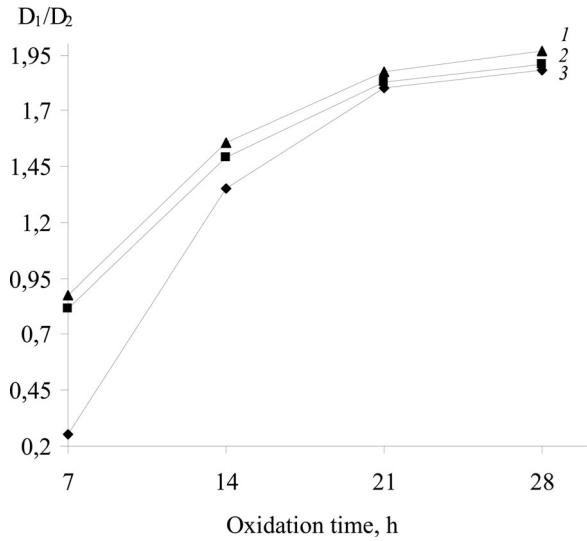


Figure 1. Kinetic curves of the oxidation of paraffinic oil in the presence of antioxidants (C_{AO} = 0.25% wt, T = 180°C): *1* – Agidol-5, *2* – Ionol, *3* – phosphite **1**.

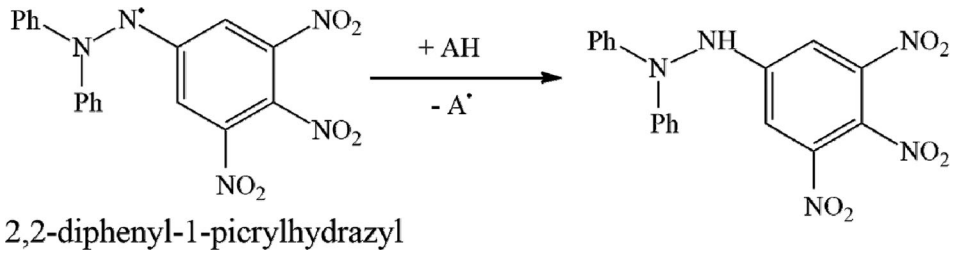
Table 1. Characteristics of the stabilizers efficiency in the oxidation conditions of industrial oil (I40A).

Compounds	A_{lmw} 10^3, mg	*AN*, mg	m, g
Unstabilized oil	46.6	6.9	4.22
Phosphite **1**	1.0	0.5	0.02
Irganox 1010	1.6	0.7	0.19
Ionol	19.0	3.8	0.93
Agidol 5	2.9	1.1	0.05

Fixing the decrease in optical density at a 517 nm of 2,2-diphenyl-1-picrylhydrazyl solution with an antioxidant in time, we calculated the rate constant of the interaction of phosphite **1** with 2,2-diphenyl-1-picrylhydrazyl: k_2, which amounted to 9.37 $\times 10^{-2}$ mol/L·s. The obtained value of k_2 indicates a high antiradical activity of phosphite **1**, which correlates well with the antioxidant activity.[7]

Experimental

All operations were performed in an argon atmosphere. NMR spectra were recorded with a Bruker Avance 600



2,2-diphenyl-1-picrylhydrazyl

Scheme 2. Reaction mode of 2,2-diphenyl-1-picrylhydrazyl.

spectrometer (Germany). Elemental analysis was performed with a Euro EA 3000 instrument (Italy). 2,6-Di-*tert*-butyl-4-(3-hydroxypropyl)phenol (**2**) was synthesized according to literature method.[8] 2,2-diphenyl-1-picrylhydrazyl (Sigma-Aldrich Chemie, Germany), reference antioxidants, paraffinic (GOST 3164-78), and mineral (GOST 20799-88) oils were used without further purification. 1,4-Dioxane was dried according to literature method,[9] the water content in 1,4-dioxane was not more than 50 ppm.

The noncatalytic oxidation of paraffinic oil with oxygen was carried out in a VTI apparatus (GOST 981-75) at 180 °C for 35 h and an oxygen supply rate of 120 mL/min. The content of antioxidant additives in liquid paraffinic oil was 0.25% by weight. IR spectra of samples of oxidized paraffinic oil were recorded on a Perkin Elmer Spectrum Two FT-IR spectrometer (USA).

The catalytic oxidation of mineral oil with oxygen was carried out in a VTI apparatus (GOST 981-75) at 170 °C for 5 h and an oxygen supply rate of 120 mL/min. The content of antioxidant additives in liquid mineral oil was 0.25% by weight.

The kinetics of the interaction of antioxidants with 2,2-diphenyl-1-picrylhydrazyl under study was investigated with a Lambda 35 spectrophotometer (Perkin Elmer, USA) with a Peltier thermostat (Perkin Elmer, USA) using the time variation of 2,2-diphenyl-1-picrylhydrazyl optical density at 517 nm (absorption maximum). Initial concentrations: 2,2-diphenyl-1-picrylhydrazyl $\sim 10^{-5}$ mol/L, antioxidants — 0.01 – 0.02 mol/L. The reaction was carried out to the degree of conversion of 2,2-diphenyl-1-picrylhydrazyl of 50%. In the control experiment, it was shown that the concentration of 2,2-diphenyl-1-picrylhydrazyl solution in 1,4-dioxane does not change when it is irradiated in a cell for an hour. The rate constant for the interaction of the reference antioxidant Ionol under the indicated conditions was 7.06×10^{-2} mol/(L·s). The Supplemental Materials contains sample ^{1}H, ^{13}C and ^{31}P NMR spectra for **1** (supporting information Figures S1–S3).

Bis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propyl)phosphite (1)

A mixture of 2,6-di-*tert*-butyl-4-(3-hydroxypropyl)phenol (**2**) (59.9 g, 0.23 mol), dibutyl phosphite (**3**) (22.0 g, 0.11 mol) and metallic sodium (0.05 g, 0.0022 mol) was gradually heated in a round-bottomed flask with stirring, ensuring that the temperature of the distillate in the vapor was not higher than 75–77 °C. The reaction was completed after the distillation of *n*-butyl alcohol reached an amount close to the theoretically calculated value. The resulting reaction mass was purified from unreacted volatile substances by distillation *in vacuo* at a pressure of 5 mm Hg at a temperature of 300 °C in Wood's bath to give **1** as viscous transparent light-yellow liquid. The yield of synthesized phosphite (**1**) was 91.6%. ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta = 1.42$ (s, 18H, *t*-Bu), 1.97–2.01 (m, 2H, CH_2), 2.61–2.65 (m, 2H, CH_2), 4.10–4.13 (m, 2H, CH_2), 6.97 (s, 2H, arom-H). ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta = 30.4$ (CH_3), 31.7 (CH_2), 32.5 (CH_2), 34.3 (CMe_3), 65.3 (d, $^{2}J_{PC} = 10.4$ Hz, OCH_2), 124.9 (arom-C), 131.4 (arom-C), 136.0 (arom_C), 152.1 (arom-C). ^{31}P NMR ($CDCl_3$, 160 MHz): $\delta = 9.5$ (d, $^{1}J_{PH} = 686$ Hz). Elemental analysis for $C_{34}H_{53}O_5P$: Found: C 71.10; H 9.58, P 5.40, O 13.92. Calcd.: C 71.30, H 9.33, P 5.41, O 13.97%.

Conclusions

By transesterifying of *n*-dibutylphosphite with 2,6-di-*tert*-butyl-4-(3-hydroxypropyl)phenol, new bis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propyl)phosphite **1** was synthesized. The high antioxidant activity of **1** was demonstrated by different methods in a model reaction with 2,2-diphenyl-1-picrylhydrazyl.

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